

# THE ANALYST

PROCEEDINGS OF THE SOCIETY FOR ANALYTICAL CHEMISTRY

## DEATH

WE record with regret the death of

William Wilson.

## NORTH OF ENGLAND SECTION

THE Nineteenth Summer Meeting of the Section was held at the Imperial Hotel, Llandudno, from Friday, June 15th, to Monday, June 18th, 1956.

The Chairman of the Section, Mr. J. R. Walmsley, A.M.C.T., F.P.S., F.R.I.C., presided. On the morning of Saturday, June 16th, Mr. F. L. Okell, F.R.I.C., Advisory Editor of *The Analyst*, gave a talk entitled "Some Memories of the Last Fifty Years," in which he outlined the part played by the Society and its members in the advancement of analytical chemistry during the last half-century.

## WESTERN SECTION

THE Summer Meeting of the Section was held at Bath from Friday, June 1st, to Monday, June 4th, 1956.

The scientific session was opened on Saturday, June 2nd, in the Pump Room by the Mayor of Bath, Councillor S. A. Smith. Mr. H. N. Wilson, F.R.I.C., introduced the film "The Technique of Sampling" (Imperial Chemical Industries Ltd.), which shows the general principles of sampling and the application of those principles to manual and automatic sampling.

When the film had been shown, the following papers were presented and discussed: "Sampling with Regard to Foods and Drugs," by A. Tyler, M.B.E., F.R.S.H., F.S.I.A. (Chief Sanitary Inspector of the City of Bath); "A Few Comments on the Administration of the Fertilisers and Feeding Stuffs Act," by C. J. Sears, M.I.W.M.A. (Chief Inspector of Weights and Measures, Wiltshire County Council).

After lunch in the Pump Room, a visit was paid to the Roman Baths and Guildhall, and in the evening a dinner was held at the Vineyard, Colerne, near Bath. On the Sunday afternoon, members and their guests were taken on a coach tour of Limpley Stoke, Bradford-on-Avon, Lacock and Lacock Abbey, returning via Castle Coombe to Bath.

## A Comparative Study of Three Recently Developed Polarographs

By D. J. FERRETT, G. W. C. MILNER, H. I. SHALGOSKY AND L. J. SLEE  
*(Presented at the meeting of the Physical Methods Group on Tuesday, February 14th, 1956)*

The recently developed instruments include the cathode-ray polarograph, the square-wave polarograph and the Cambridge Univector polarograph unit. These instruments have been tested to obtain information on their relative merits and details of the results obtained are described. The tests included the following aspects: (i) sensitivity for reversible and irreversible reductions at the dropping-mercury electrode, (ii) resolution for elements with half-wave potential values very close together, (iii) effects of the reduction of a major constituent at a more positive potential on the determination of a minor constituent, and (iv) speed of application, reproducibility and usefulness in analytical chemistry.

DESPISE statements about the relative merits of high-sensitivity derivative polarographs,<sup>1,2</sup> no comparative study of their behaviour has been made.

A series of solutions has, therefore, been examined by using three polarographs that are more sensitive than those hitherto available commercially.

These instruments are—

- (a) the Univector unit, manufactured by Cambridge Instrument Co. Ltd.,
- (b) the Mervyn - Harwell square-wave polarograph, manufactured by Mervyn Instruments, and
- (c) the single-sweep cathode-ray polarograph, manufactured by Southern Instruments Ltd.

These will be referred to as CU, SWP and CRP, respectively, in this paper.

The CU unit in conjunction with a conventional polarograph produces derivative polarograms, and the Cambridge Instrument Co. Ltd. claim that it increases the sensitivity of such an instrument by a factor of up to twentyfold.<sup>3</sup> For these tests, the CU was coupled to a Cambridge pen-recording polarograph. The SWP produces only derivative polarograms. The CRP used was the original instrument constructed by Davis and Seaborn,<sup>4</sup> but an almost identical instrument is now manufactured by Southern Instruments Ltd. This polarograph will give both its own typical polarogram (which is in fact semi-derivative) and the derivative of this. Whenever possible, both types of waves were obtained and recordings were made by using a 35-mm oscilloscope camera.

### EXPERIMENTAL

For derivative polarograms it is not necessary to remove oxygen from the solutions except for the high-sensitivity settings of all three instruments. For normal polarograms on the CRP and Cambridge polarographs, however, the solutions must be free from dissolved oxygen. This was ensured by passing hydrogen through the solution for at least 10 minutes before polarograms were recorded.

For examination with the SWP and CU, the base electrolyte must not be less than  $M$ , so that the electrical resistance of the cell shall be small. The CU and CRP use any ordinary polarographic cells, but, for the best results at low concentrations, the SWP requires a specially constructed cell in which the drops of mercury do not fall into the anode. The CRP and SWP require the leads to the electrodes to be screened.

### RESULTS

#### SENSITIVITY—

(a) *For reversible reductions*—A solution containing 0.18  $\mu\text{g}$  of cadmium per ml in  $M$  hydrochloric acid was studied, the results being shown in Fig. 1. The peak heights of the cadmium waves measured were—

SWP	..	..	240 mm at maximum sensitivity
normal CRP	..	..	40 mm at 1/5 maximum sensitivity
derivative CRP	..	..	5 mm at maximum sensitivity
CU	..	..	20 mm at maximum sensitivity

normal Cambridge polarograph just visible, say 1 mm, at maximum sensitivity.

The base-line with the normal CRP presentation at 1/5 maximum sensitivity sloped so steeply that it was not possible to measure the peak height at any sensitivity greater

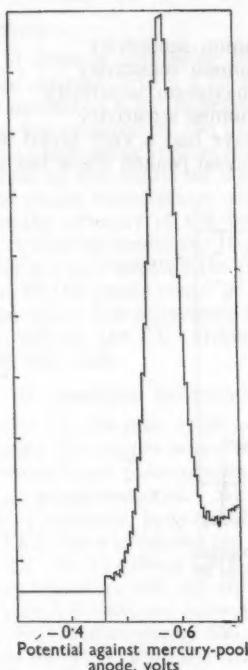


Fig. 1 (a). Square-wave polarogram for a 0.18  $\mu\text{g}$  per ml solution of cadmium in  $M$  hydrochloric acid

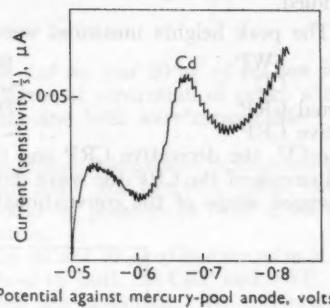


Fig. 1 (b), part 1. Cathode-ray polarogram for a 0.18  $\mu\text{g}$  per ml solution of cadmium in  $M$  hydrochloric acid. Normal polarogram

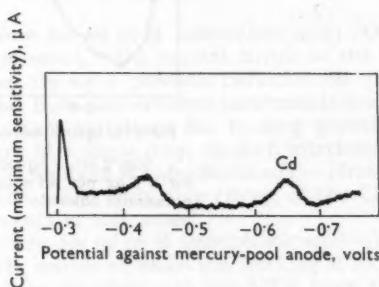


Fig. 1 (b), part 2. Cathode-ray polarogram for a 0.18  $\mu\text{g}$  per ml solution of cadmium in  $M$  hydrochloric acid. Derivative polarogram

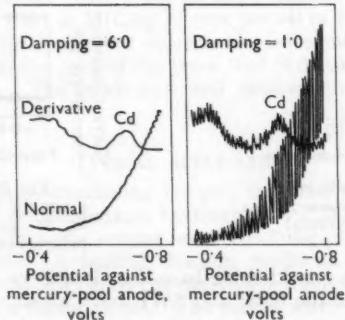


Fig. 1 (c). Univector polarograms for a 0.18  $\mu\text{g}$  per ml solution of cadmium in  $M$  hydrochloric acid

than this. (One cause of the sloping base line is the presence of impurities in the base electrolyte and since for comparative tests all solutions were  $M$  such interference was unavoidable.) With more dilute electrolytes it is possible to increase the usable peak height.

The ratios of peak heights measured were: normal polarograph to derivative CRP to CU to normal CRP to SWP = 1 to 5 to 20 to 40 to 240.

(b) *For irreversible reductions*—

(i) A solution containing 5  $\mu\text{g}$  of nickel per ml in  $M$  potassium chloride solution was studied.

The peak heights measured were—

SWP	..	..	..	90 mm at maximum sensitivity
CU	..	..	..	~ 2 mm at maximum sensitivity
normal CRP	..	..	..	50 mm at 1/5 maximum sensitivity
derivative CRP	..	..	..	~ 2 mm at maximum sensitivity.

On the CU, the derivative CRP and the SWP the wave had a very broad base. On the normal circuit of the CRP the wave did not have the usual peaked shape but was more like the stepped shape of the conventional polarogram.

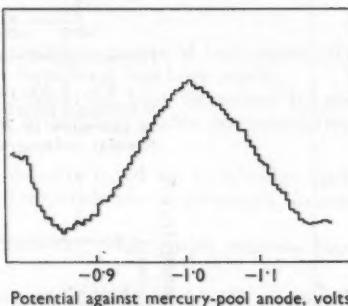


Fig. 2 (a). Square-wave polarogram for a 5  $\mu\text{g}$  per ml solution of nickel in  $M$  potassium chloride

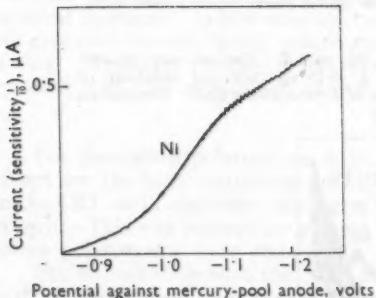


Fig. 2 (b), part 1. Cathode-ray polarogram for a 5  $\mu\text{g}$  per ml solution of nickel in  $M$  potassium chloride. Normal polarogram

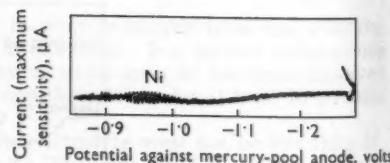


Fig. 2 (b), part 2. Cathode-ray polarogram for a 5  $\mu\text{g}$  per ml solution of nickel in  $M$  potassium chloride. Derivative polarogram

With the CRP there is a considerable base-line slope even at one-fifth maximum sensitivity and it is apparent that the CRP and SWP have about similar sensitivities with this reduction (see Fig. 2).

(ii) A solution of Pontachrome violet SW (2-hydroxy-5-sulpho- $\alpha$ -benzeneazo-2-naphthol) containing 2  $\mu\text{g}$  of aluminium per ml was used.

The peak heights obtained were—

CU	..	..	29 mm at 1/10 maximum sensitivity
SWP	..	..	180 mm at 1/20 maximum sensitivity
normal CRP	..	..	27 mm at 1/1000 maximum sensitivity.

This is obviously a highly irreversible reduction, as the CRP is more sensitive than the SWP, despite the fact that four electrons are involved in the reduction of the aluminium dye. This should favour the SWP, for the peak height with this instrument varies with  $n^2$ , whereas with the CRP it varies with  $n^{3/2}$ .

#### RESOLUTION—

(a) *A solution containing 20 µg of cadmium per ml and 20 µg of indium per ml in M potassium chloride*—For a 1 to 1 mixture the degree of separation of peaks with the SWP and the derivative CRP appeared to be the same and both were measurable. The double peak was not resolved by the CU.

For a cadmium to indium ratio of 10 to 1 the indium wave could be detected as a swelling at the base of the cadmium wave with both the SWP and the CU. With the derivative CRP the peaks were clearly separated. It would be possible in both cases to make an approximate estimate of the indium concentration.

(b) *A solution containing 10 µg of thallium per ml and 10 µg of lead per ml in M hydrochloric acid*—For a 1 to 1 mixture the peaks were resolved by both the CRP and SWP. At 10 to 1 and 1 to 10 the peaks could be distinguished but not measured. We estimate that 7 to 1 would be about the maximum ratio that could be measured. Once again the peaks were not resolved by the CU, although the presence of two reductions was evident from the shape of the peak.

#### EFFECT OF PREVIOUS REDUCTIONS—

(a) *Fe<sup>+++</sup> to Cu ratio of 20 to 1 (1 mg of iron per ml in M hydrochloric acid)*—On all three instruments the copper wave was readily measured. The normal circuit of the CRP, like most conventional polarographs, can compensate for a previous reduction 50 times larger than that being measured. Such polarograms from conventional instruments are, however, difficult to measure, because of the large current variations due to drop growth and fall. As the CRP trace is carried out in the lifetime of a single drop, no such interference occurs.

(b) *Fe<sup>+++</sup> to Ni ratio of 100 to 1 (1 mg of iron per ml in M hydrochloric acid)*—Here, the nickel peak was observed with all three instruments. The derivative circuit of the CRP was of course used for this and subsequent experiments in this series.

(c) *Fe<sup>+++</sup> to Cu ratio of 333 to 1 (1 mg of iron per ml in M hydrochloric acid)*—The copper wave was visible on both the CU and the SWP, neither of which was working at its maximum sensitivity. In fact, the copper wave has been detected with the SWP when the iron to copper ratio was 5000 to 1.

The CRP could not be used above one-fifth of its maximum sensitivity because the cell current due to the iron reduction was so large that the voltage drop in the higher values of cell-load resistors was greater than could be compensated by the voltage-sweep circuit.

(d) *Fe<sup>+++</sup> to Bi ratio of 1000 to 1 (1 mg of iron per ml in M hydrochloric acid)*—With the CRP the bismuth peak was visible but not measurable, since, owing to its very early reduction potential, the wave occurs on the part of the trace that is distorted when the potential passes through zero applied volts. The peak was well defined and measurable with the SWP but not with the CU.

#### TYPICAL APPLICATIONS

(a) A solution of a bronze containing copper, zinc and nickel in the ratios 86 to 1.86 to 0.04 was prepared in a *M* ammonium hydroxide - *0.2 M* ammonium chloride solution. An initial solution in which the copper level was 5 mg per ml did not give good results with any of the instruments. A tenfold dilution produced peaks for nickel and zinc on both the SWP and CRP, although, since the derivative circuit was used, the SWP was more sensitive than the CRP by a factor of 20. The nickel wave was not visible on the CU, as might be expected, since the concentration of nickel was only 0.5 µg per ml.

(b) A Mazak alloy containing copper, lead, cadmium and indium was examined. With all three instruments the Cu<sup>+</sup> and Pb<sup>++</sup> peaks were easily measured. With the CRP, the

indium peak was sufficiently resolved to permit a direct measurement of the indium concentration to be made with an accuracy of about 10 per cent. The resolution with the SWP and the CU was not sufficient to permit a direct measurement (see Fig. 3).

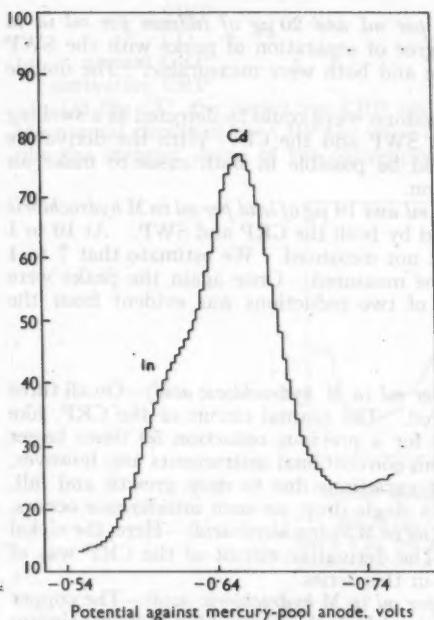


Fig. 3 (a). Square-wave polarogram for Mazak alloy in chloride solution

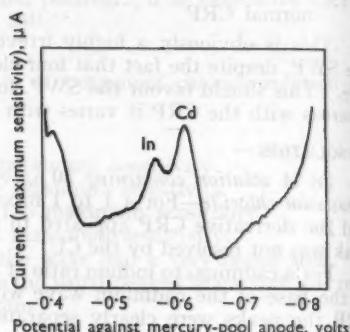


Fig. 3 (b). Cathode-ray polarogram for Mazak alloy in chloride solution

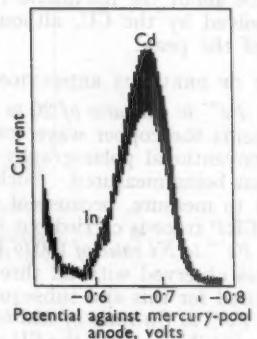


Fig. 3 (c). Univector polarogram for Mazak alloy in chloride solution

## DISCUSSION

In the analysis of solutions containing a single cation at dilutions up to ten times those normally employed in polarography, there is little to choose between the CRP and the SWP. At greater dilutions, however, the slope of the base line of the CRP trace increases and finally sets a limit to the amplifier gain that can usefully be employed. This slope may be largely eliminated by means of the derivative circuit, but the signal then obtained is about 25 times less than before. At very low concentrations there is insufficient reserve of gain available in the present model to enable the signal loss to be fully overcome. Considerations of ease and accuracy of peak measurement may well, however, dictate the use of the derivative technique.

The CU suffers from base-line irregularities at high sensitivities, but it must be pointed out that the manufacturers recommend that sensitivities greater than one-fifth maximum should not be employed. The derivative trace was, however, much easier to measure than that produced by the normal polarograph.

The SWP is virtually free from base-line difficulties, even at maximum sensitivity. With the SWP and CU the base electrolyte must be extremely pure as a concentration of 1 molar has to be used. With the CRP the base electrolyte can be very dilute, with the consequent reduction in the difficulties caused by impurities.

## SPEED—

The CRP has an advantage in that an immediate scan over its potential range of 0.5 volt is made every 7 seconds. The CU and SWP have a slow recorder type presentation.

The greatest care over deoxygenation is necessary only at high sensitivities of the CU and CRP. Bubbling pure hydrogen through for 20 minutes is generally essential to ensure freedom from oxygen interference. With the SWP it is rarely necessary to deoxygenate for more than 3 minutes. Thus the total time for polarography of a single solution is about the same for the CRP and SWP. If polarograms have to be recorded for many solutions, however, the solutions may be deoxygenated simultaneously and ten solutions may readily be dealt with in 30 minutes on the CRP.

## ACCURACY OF PEAK-HEIGHT MEASUREMENT—

The CRP trace can have a width as small as approximately 0.2 mm. The peak height can therefore be measured over a maximum height of 100 mm with an accuracy of  $\pm 0.5$  per cent. The SWP, with a thin ink line over 280 mm, is obviously more accurate than this. The CU has a maximum chart height of 75 mm, and for the best resolution damping should not be used. However, when care was taken, the results appeared to be as accurate as those produced by the other two presentations.

## REPRODUCIBILITY—

With all three instruments, the limitation in reproducibility appears to be due to variations of the capillary characteristics. Thus the SWP and the CU (on sensitivities less than one-fifth) may give slightly differing results from successive polarograms of the same solution. At sensitivities greater than one-fifth the CU results may vary much more. The CRP presents a trace that appears to be identical for successive drops. If the drop-time should change, then the drop fall is observed to occur at a different place on the screen. It is, therefore, easier to observe a change in the drop-time with the CRP than with the SWP or CU.

## MAINTENANCE—

The CRP has been in everyday use at Woolwich for 5 years with only one major breakdown. The CU and pen-recording polarograph both have electronic amplifiers, but are unlikely to be more troublesome than normal polarographs.

The SWP is a more recent development and long term testing has not been possible, but experience has shown that 6 months is a reasonable trouble-free period.

## CONCLUSIONS

The sensitivity and resolution of three recently designed polarographs have been compared. Typically reversible and irreversible reductions have been studied. While it is hoped that the results are representative, it must be borne in mind that the relative behaviour of these instruments may vary considerably from one electrode reduction to another.

## SENSITIVITY—

The SWP is the most sensitive of the polarographs for the study of a reversible reduction, e.g., cadmium. It is 6 times as sensitive as the normal CRP trace, 12 times as sensitive as the CU, 40 to 50 times as sensitive as the derivative CRP and more than 200 times as sensitive as a conventional polarograph. The CRP loses less in sensitivity when studying irreversible reductions than does the SWP.

## RESOLUTION—

The CRP on its derivative circuit has a rather better resolving power than the SWP.

## EFFECT OF PREVIOUS REDUCTIONS—

The SWP is less affected by earlier reductions than the CRP and CU and can deal<sup>5</sup> with ratios of 20,000 to 1. The maximum ratio that can be examined with the CRP is 400 to 1. With the CU the maximum ratio is about 800 to 1.

## REFERENCES

1. Reynolds, G. F., *J. Polarographic Soc.*, 1955, **1**, 17.
2. Lamb, B., *Evershed News*, 1956, **4**, 16.
3. "The Cambridge Univector Polarograph Unit," Cambridge Instrument Co. Ltd., London, 1953.
4. Davis, H. M., and Seaborn, J. F., *Electronic Eng.*, 1953, **25**, 314.
5. Ferrett, D. J., and Milner, G. W. C., *Analyst*, 1956, **81**, 193.

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RESEARCH GROUP

WOOLWICH OUTSTATION, WOOLWICH, S.E.18

March 22nd, 1956

## The Polarographic Determination of Uranium

By H. I. SHALGOSKY

(Presented at the meeting of the Physical Methods Group on Tuesday, February 14th, 1956)

A published method for the polarographic determination of uranium in an acid tartrate medium has been examined. Under the conditions that were adopted to achieve maximum sensitivity, the method has been shown to give low results. This is due to the effect of heating uranium in concentrated sulphuric acid solution. Satisfactory results are obtained when perchloric acid is used for the chemical treatment and the dilute sulphuric acid is added to the cold solution immediately before the polarographic determination.

The sensitivity of the final method is shown to be similar to those of other polarographic methods for the determination of uranium, and the factors that affect sensitivity are discussed.

A METHOD for the polarographic determination of uranium in ores was recently published by Legge,<sup>1</sup> who claims that his method is more sensitive than others. He rejects the acid tartrate medium recommended by Lewis and Overton<sup>2</sup> on the grounds that it lacks sensitivity, even though fewer elements interfere with the determination in this medium. However, the data he presents to justify his choice of base electrolyte appear to be theoretically unsound.

Since a sensitive method for the determination of uranium was required, it was decided to investigate this matter. Some of the experimental work will be given in detail, because of the unusual nature of the difficulties encountered.

## EXPERIMENTAL

The Cambridge pen-recording polarograph used had a maximum sensitivity of  $0.0026 \mu\text{A}$  per mm. The dropping-mercury electrode had a capillary characteristic of  $2.68 \text{ mg}^{2/3} \text{ sec.}^{-1/2}$  in 2 N potassium chloride with no applied potential. All solutions were deoxygenated with electrolytically generated hydrogen and polarograms were recorded at  $25^\circ \pm 0.1^\circ \text{C}$ , a mercury pool being used as anode. All reagents were of analytical-reagent quality and were polarographically checked for purity. Doubly distilled water was used throughout. A standard solution containing 100 mg of uranium per ml was available. This had been prepared by dissolving pure uranium metal in nitric acid. Uranyl sulphate solutions were prepared by heating aliquots of the nitrate solution to fuming with sulphuric acid and diluting to volume with water. A 0.1 per cent. w/v solution of proteose peptone containing 0.2 per cent. w/v of redistilled phenol as preservative was used as a maximum suppressor, being diluted 100-fold in use. A tartrate stock solution was prepared by dissolving 15 g of Rochelle salt in water, adding 10 ml of saturated potassium chloride solution and 10 ml of proteose peptone solution, and making up to 100 ml with water.

## RELATIVE SENSITIVITIES OF THE TARTRATE AND OXALIC ACID BASE ELECTROLYTES—

The diffusion current constant,  $I$ , which is given by the equation—

$$I = \frac{i_d}{cm^{2/3} f^{1/6}}$$

where  $i_d$  = diffusion current in  $\mu\text{A}$ ,  $c$  = concentration of uranium in millimoles per litre, and  $m^{2/3} l^{1/6}$  = capillary characteristic as  $\text{mg}^{2/3} \text{sec.}^{-1/2}$ , was measured, with use of the two base electrolytes that were to be compared. A 1.0-ml aliquot of a standard uranyl nitrate solution containing 100  $\mu\text{g}$  of uranium per ml was placed in a 5-ml calibrated flask, and 1.0 ml of 5  $M$  sulphuric acid and 0.5 ml of tartrate stock solution were added. The solution was made up to the mark and a polarogram was recorded. The diffusion constant was 2.66.

The second solution contained 1  $\mu\text{g}$  of uranium per ml, and was 0.5  $M$  in oxalic acid and 0.9  $M$  in sulphuric acid. The diffusion-current constant at this concentration of uranium was 2.31.

Hence, the tartrate base electrolyte is of comparable sensitivity with the oxalic acid base recommended by Legge, and further work was therefore confined to the tartrate medium, as fewer elements interfere.

#### EFFECT OF BASE-ELECTROLYTE COMPOSITION—

A calibration graph was prepared with use of the tartrate base electrolyte and the procedure outlined above, and samples containing known amounts of uranium were then examined. In order to eliminate interference from the gross amounts of nitrate ion present, the samples were evaporated to fuming with 1.0 ml of 5  $M$  sulphuric acid and washed into a 5-ml calibrated flask, 0.5 ml of tartrate stock solution was added, the solution was made up to the mark and polarograms were recorded. As the results were not consistent, the effect of variations of the concentration of sulphuric acid in the final solution on the diffusion current due to 20  $\mu\text{g}$  of uranium per ml was studied, with the results shown in Table I.

TABLE I

#### EFFECT OF SULPHURIC ACID CONCENTRATION ON DIFFUSION CURRENT

Concentration of sulphuric acid, $M$ ..	0.2	0.4	0.6	0.8	1.0	2.0	3.0
Diffusion current, $\mu\text{A}$ ..	..	0.494	0.540	0.572	0.591	0.598	0.572

The optimum concentration of sulphuric acid for maximum sensitivity was therefore 1.0  $M$ . It was obvious, however, that care must be taken to ensure that as little acid as possible was lost by fuming in order to maintain a uniform acid concentration.

A  $\pm 10$  per cent. variation in the concentration of the tartrate solution was found to have no measurable effect on the uranium diffusion current.

Determinations carried out on the sample of known content were now about 10 per cent. low. Since the only difference between the sample and standard solutions was that the former had been heated with sulphuric acid, the experiments described below were carried out.

#### EFFECT OF HEATING—

Aliquots of uranyl nitrate solution were heated with 1 ml of 5  $M$  sulphuric acid at 400°C in an air-bath for about 20 minutes. The solutions were then washed into 5-ml calibrated flasks, 0.5 ml of tartrate stock solution was added to each, and the mixtures were made up to the mark and polarograms were recorded.

Duplicate results are shown in Table II, together with those for a series of solutions that had not been heated.

TABLE II

#### EFFECT OF HEATING URANIUM WITH SULPHURIC ACID

Uranium added, $\mu\text{g}$	Uranium recovered, $\mu\text{g}$		
	Unheated solution	Heated solution	Heated solution
60	62	58	59
100	102	92	70
180	176	142	157

Standard additions of uranium to solutions giving low recoveries, and to unheated solutions, gave almost identical increases in height, equal to those expected from unheated solutions. No difference was detected between heated and unheated solutions containing

no uranium. Addition of sodium nitrate to solutions that had been heated did not affect the uranium diffusion current; nor did substitution of uranyl sulphate for uranyl nitrate. It was noted during these experiments, however, that the diffusion current from heated solutions slowly increased with time, and the results in Table III were therefore obtained.

TABLE III

## VARIATION WITH TIME OF STEP HEIGHT FOR HEATED SOLUTIONS

Time after dilution, minutes	0	20	120	140	Unheated solution
Diffusion current, $\mu\text{A}$	0.462	0.514	0.553	0.565	0.565

In order to test whether this phenomenon occurred when the base electrolyte recommended by Legge<sup>1</sup> was used, a heated uranium in sulphuric acid solution was made up with oxalic acid such that the final solution was 0.5 M in oxalic acid and 0.9 M in sulphuric acid. The diffusion current obtained was only two-thirds of that found from a similar solution prepared without heating, but increased to the same value after the solution had been set aside overnight.

As it was undesirable to wait for nearly 3 hours to obtain reproducible results, the use of sulphuric acid for the removal of nitrate ion was abandoned in favour of 0.5 ml of 60 per cent. perchloric acid, which is known to be a non-complexing medium for uranium. The sulphuric acid, which must still be present, however, was now added to the cold sample solution in the 5-ml calibrated flask after the tartrate and uranium solutions had been mixed. The presence of perchloric acid precluded the use of potassium salts in the base electrolyte, and a new stock solution was prepared for use in all subsequent experiments involving the tartrate medium.

This stock solution contained 12 g of disodium tartrate,  $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$ , 10 ml of proteose peptone solution and 0.293 g of sodium chloride per 100 ml. The effect of variations in the composition of the base electrolyte on the diffusion current due to 20  $\mu\text{g}$  of uranium per ml is shown in Table IV.

TABLE IV  
EFFECT OF BASE-ELECTROLYTE COMPOSITION

Amount of 60 per cent. perchloric acid, ml	Amount of 5 M sulphuric acid, ml	Amount of tartrate solution, ml	Diffusion current, $\mu\text{A}$
0.25	1.0	0.5	0.546
0.5	1.0	0.5	0.579
1.0	1.0	0.5	0.591
0.5	0.9	0.5	0.546
0.5	1.1	0.5	0.572
0.5	1.0	0.45	0.565
0.5	1.0	0.55	0.559

Since the concentration of perchloric acid in the final solution is important, the procedure adopted to remove nitrate ion was to evaporate the uranium in perchloric acid solution down to 0.1 ml and add 0.4 ml of 60 per cent. perchloric acid. After this treatment the diffusion current fell to 0.494  $\mu\text{A}$ , but in contrast to the effect of sulphuric acid, it was quite reproducible. Further, no change was observed with time, even when the solution was set aside overnight.

A calibration graph was prepared by using solutions of uranium in perchloric acid that had been heated. The graph was slightly curved at its lower end, but was almost linear over the range 20 to 200  $\mu\text{g}$  of uranium per ml.

Determinations on samples of known uranium content were satisfactory and agreed with results obtained absorptiometrically.

## INTERFERENCES—

It was known that bismuth, copper, lead and molybdenum are reduced at potentials close to that of uranium in the tartrate medium and the half-wave potentials of these elements are shown in Table V, together with the values for uranium in the oxalic acid base electrolyte and in N sulphuric acid.

Only the molybdenum wave was sufficiently close to that of uranium to interfere, and therefore it must not be present in sample solutions. Lewis and Overton<sup>2</sup> reported that the concentration of nitrate ion in the final solution must be less than 0.1 M.

TABLE V  
HALF-WAVE POTENTIALS

Element	Medium	$E_{1/2}$ , volts against the saturated-calomel electrode
Uranium	tartrate	-0.44
Bismuth	tartrate	-0.28
Copper	tartrate	-0.29
Molybdenum	tartrate	-0.49
Lead	tartrate	-0.66
Uranium	oxalic acid	-0.33
Uranium	N sulphuric acid	-0.42

### METHOD

#### REAGENTS—

*Sulphuric acid*, 5 M—Add 100 ml of 18 M sulphuric acid to 200 ml of cold water, cool and dilute to 360 ml with water.

*Proteose peptone solution*, 0.1 per cent. w/v—Dissolve 0.1 g of proteose peptone and 0.2 g of phenol in 100 ml of water.

*Disodium tartrate stock solution*—Dissolve 12.0 g of disodium tartrate,  $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$ , and 0.293 g of sodium chloride in water, add 10 ml of 0.1 per cent. proteose peptone solution and dilute to 100 ml with water.

#### PROCEDURE—

The uranium should be in perchloric acid solution and free from molybdenum. Evaporate the perchloric acid down to 0.1 ml and add 0.4 ml of 60 per cent. perchloric acid. Transfer the solution to a 5-ml calibrated flask and add washings of the sample container, using a total of about 2 ml of water (a dropper pipette is most convenient for this). Add 0.5 ml of disodium tartrate stock solution to the calibrated flask, set aside for about 2 minutes and then add 1.0 ml of 5 M sulphuric acid. Make up to the mark with further washings of the sample container, place the stopper in the flask and shake. Transfer the solution to a polarographic cell, deoxygenate it, and record a polarogram over the range 0 to -0.6 volt, using the mercury pool as anode. Measure the height of the uranium step, which occurs at a half-wave potential of -0.35 volt, using the intersection method of step-height measurement. Read off the amount of uranium in the sample from a calibration graph prepared by using known amounts of uranium in perchloric acid solution and proceeding exactly as described above.

### RESULTS

With the Cambridge pen-recording polarograph, a step-height of at least 40 mm (0.104  $\mu\text{A}$ ) can be obtained except with less than about 20  $\mu\text{g}$  of uranium. Steps can be measured to within  $\pm 0.5$  mm (0.0013  $\mu\text{A}$ ), which limits the precision of the method to  $\pm 1.5$  per cent. This was the maximum variation observed for six determinations of 100  $\mu\text{g}$  of uranium. The precision falls to  $\pm 3$  per cent. with 10  $\mu\text{g}$  of uranium, giving a step-height of  $20 \pm 0.5$  mm ( $0.052 \pm 0.0013 \mu\text{A}$ ), and this is considered to be the limit of determination of the method. The limit of detection is about 2  $\mu\text{g}$  of uranium.

Determinations have been carried out on solutions of uranium separated from ores of known composition, and the results will be given elsewhere,<sup>3</sup> with full details of the method, including the separation.

### DISCUSSION OF RESULTS

#### SENSITIVITY—

From the value of the diffusion current constant,  $I$ , it is possible to calculate the number of electrons,  $n$ , involved in a reduction at the dropping-mercury electrode. From the Ilković equation—

$$n = \frac{i_d}{605 D^{\frac{1}{2}} m^{2/3} t^{1/6} c} = \frac{I}{605 D^{\frac{1}{2}}}$$

where  $D$  = diffusion coefficient. If the value of the diffusion coefficient of uranium is assumed to be  $0.60 \times 10^{-5} \text{ cm}^2 \text{ sec.}^{-1}$ , then from the value  $I = 1.02$  in acid tartrate given by Legge,  $n = 0.69$ . This is absurdly small. We find  $n = 1.8$  from the value  $I = 2.66$  in tartrate medium, which compares well with Legge's value  $I = 2.73$  in oxalic acid medium. The discrepancy in Legge's data may be partly due to the effect of heating uranium with sulphuric acid, although it is unlikely that such treatment would reduce the diffusion current to a point where the number of electrons taking part in the reaction fell below 1.0.

#### BASE-ELECTROLYTE COMPOSITION—

Sheel and Watters<sup>4</sup> have shown that in sulphuric acid alone the diffusion current of uranium is dependent on the concentration of the sulphate ion, and that the optimum concentration of the acid for maximum diffusion current is  $1.5 \text{ N}$ .

The variations of diffusion current for uranium shown in Table I were not, therefore, entirely unexpected, although Lewis and Overton reported that sulphate ion had no effect on the tartrate method. It is possible that the variations observed were due solely to differences in hydrogen-ion concentration, but the results in Table IV indicate that both the sulphate-ion concentration and the hydrogen-ion concentration affect the diffusion current.

It is obvious that for a routine method, the sulphuric acid and perchloric acid concentrations should be carefully controlled.

The diffusion-current constants for the three media, sulphuric acid alone, and with oxalic acid and disodium tartrate present are remarkably similar, being 2.75, 2.73 and 2.66, respectively. Now the reduction of the simple uranyl ion—



can be followed by the disproportionation—



This disproportionation occurs more readily if the products are stabilised by complex formation, but this will also cause a shift in the half-wave potential of reduction (1) if the  $\text{U}^{\text{IV}}$  species resulting from this reduction remain complexed, then the prime factor in driving reaction (2) to the right becomes the complexing of the  $\text{U}^{\text{IV}}$  species.

Hence, although the  $\text{U}^{\text{VI}}$  is complexed to different extents in the three media considered (as shown by the half-wave potential in Table V), the similarity of the diffusion-current constants indicates the the  $\text{U}^{\text{IV}}$  sulphate complex is stronger than those with oxalic acid and disodium tartrate.

In support of this, Legge has shown that the diffusion current of uranium in the presence of sulphuric acid is independent of the oxalic acid concentration over the range 0.1 to  $0.5 \text{ M}$ . Also, the diffusion-current constant of uranium in approximately  $0.01 \text{ M}$  hydrofluoric acid solution<sup>4</sup>, which is known<sup>5</sup> to form a strong complex with  $\text{U}^{\text{IV}}$  ( $K = 3.7 \times 10^{-14}$ ), is 2.48.

It is concluded that the addition of further complexing agents, such as oxalic acid, tartrate and citrate, to uranium in sulphate solutions assists mainly in the separation of interfering waves and hardly affects the diffusion current or the mechanism of the reactions at the dropping-mercury electrode.

Kern and Orlemann<sup>6</sup> have shown that in a non-complexing medium the rate of disproportionation is proportional to the square of the  $\text{UO}_2^{\cdot}$  concentration. The non-linearity of our calibration graph indicates that this relationship also holds in complexing media. As long as the  $n$  value of the reduction is less than 2, this non-linearity should be observed, but as the concentration of uranium is increased, so  $n$  will approach 2, and the graph will become linear. Our graph was curved over the range  $10^{-5}$  to  $10^{-4} \text{ M}$  uranium and linear over the range  $10^{-4}$  to  $10^{-3} \text{ M}$  uranium. The other constituents of the base electrolyte, *viz.*, proteose peptone and sodium chloride, take no part in the reactions. The chloride ion permits a mercury pool to be used as anode, which is convenient in a routine method. The proteose peptone stock solution is quite stable and the tartrate stock solution has given reproducible results for 3 months, although it became cloudy towards the end of this period.

#### EFFECT OF HEATING—

Further work is required before the cause of the apparent loss of uranium when it is heated with concentrated sulphuric acid can be known with any certainty. A possible explanation is that a very stable uranyl sulphate complex is formed or, what amounts to the same thing, the normal uranyl species is dehydrated and the water replaced with sulphate

ions. Such a complex, after reduction, might not disproportionate as rapidly as the normal species, but some difference in the half-wave potentials of the normal  $U^{VI}$  and the complexed  $U^{VI}$  species might be expected. No such shift has, however, been observed in these solutions.

It is not known whether the smaller and reproducible decrease of the diffusion current that occurs when uranium is heated with perchloric acid is due to a similar reason to that mentioned above. Whatever the cause, however, the effect is very important in the determination of uranium.

It must be stressed that, when sulphuric acid was used, it was not possible to produce the lowering of the diffusion current every time, and there may be some critical temperature, concentration, time or other factor of which we are unaware.

#### CONCLUSIONS

As a result of this investigation, which has been directed towards the production of a reliable and sensitive method for the determination of uranium, the following recommendations are made—

- (a) Uranium salts in concentrated sulphuric acid solution should not be strongly heated immediately before the polarographic determination.
- (b) The preparation of calibration and sample solutions should be as similar as possible, and for extreme accuracy as many points as possible at the lower end of the calibration graph should be obtained.
- (c) The tartrate base electrolyte should be used to avoid interfering waves. These recommendations have been incorporated in a method<sup>3</sup> for the determination of uranium in ores, which is rapid, accurate and covers a wide range of uranium contents.

I am indebted to Messrs. E. C. Hunt, E. A. Terry and F. E. Wild for carrying out separations of uranium from ores and to Mr. G. J. Hunter for helpful discussion.

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UNITED KINGDOM ATOMIC ENERGY AUTHORITY  
RESEARCH GROUP

WOOLWICH OUTSTATION  
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May 4th, 1956

#### DISCUSSION ON THE FOREGOING TWO PAPERS

MR. A. F. WILLIAMS asked Mr. Milner for his opinion on the superiority or otherwise of the cathode-ray polarograph over the square-wave polarograph for organic determination. He would also like to know why a change in peak height occurred as the screen was traversed and whether this change was a drawback in the use of the instrument.

MR. MILNER answered that for most organic reductions the normal circuit of the cathode-ray polarograph was possibly more sensitive than the square-wave polarograph. In reply to the second point, he said that the peak current measured with a cathode-ray polarograph was proportional to  $t_p^{2/3}$ , where  $t_p$  was the time at which the peak occurred, measured from the start of drop growth. If a peak was measured at different places on the screen, then  $t_p$  would vary, and the peak current also. For accurate quantitative work it was necessary, therefore, to use the same start potential whenever measuring a particular wave. This was not considered to be a drawback in the use of the instrument and, for routine determinations by unskilled operators, it was probably an advantage.

DR. FURNESS remarked that, when the cathode-ray polarograph waves due to the reduction of substances at the dropping-mercury electrode were displayed, the fly-back of polarising potential from negative to more positive values was triggered by the cessation of diffusion current at the instant of detachment of a drop from the capillary. For a wave due to oxidation of a substance at the dropping-mercury electrode, the change in diffusion current would be zero when the drop became detached, if the sweep were from positive to more negative potentials. He would like to know what provision was then made for triggering the fly-back, and to what extent would the shape of the wave be influenced by the diffusion current reaching

a minimum value at the instant of maximum drop size. If there were difficulties, could they be overcome by applying a voltage sweep in the direction of negative to more positive potentials, or were such difficulties avoidable simply by reversing the leads to the polarographic cell.

MR. SHALGOSKY stated that the simplest method of achieving synchronisation when the wave shape did not allow it to occur automatically was to arrange for the drop-fall to occur in the fly-back period of the instrument. He had found this to be very satisfactory. It was hoped to publish a paper describing the wave shapes obtained with reversed potential sweeps.

MR. T. R. DAVIES, on behalf of the manufacturers, stated that it should be possible to modify the cathode-ray polarograph for work on anodic oxidations.

DR. J. A. HUNTER said that, if adequate synchronisation (with cathode-ray polarography) could not otherwise be obtained in the recording of anodic waves or others in which the final current was small, it was then possible to achieve the synchronisation by manual detachment of the drop at the end of the trace. In order to obtain reproducible peak heights, in view of the dependence of peak heights on the instant during the sweep at which the peak occurred, it was essential that the trace should be accurately framed within the same voltage lines in all experiments, as otherwise the instant of occurrence of the peak would not always correspond to the same stage in the life of the drop.

DR. J. E. PAGE wished to know how sensitive the cathode-ray polarograph was in the measurement of catalytic waves, e.g., cysteine and cystine in an ammoniacal cobalt buffer solution.

MR. T. R. DAVIES replied that he had done some qualitative work with cystine and cysteine, and catalytic waves due to the evolution of hydrogen had been produced in the form of peaks. The medium had been an ammoniacal solution containing a bivalent cobalt salt.

MR. D. R. CURRY asked Mr. Milner whether the square-wave polarograph was reversible in respect of voltage scanning and what the advantages of reverse scanning were. He enquired about the advantages of increased chart size (Honeywell - Brown) as oscillations enlarged *pro rata*.

MR. G. W. C. MILNER, in reply, said that with the square-wave polarograph it was possible to use reversible voltage scanning, which was a convenience when it was necessary to record the same peak several times. Several scanning rates were available with this instrument, the maximum rate corresponding to 0.575 volt per minute and the minimum rate to 0.038 volt per minute. The Honeywell - Brown recorder in the Univector polarograph being demonstrated was not chosen purely for the convenience of its great chart size, but mainly because it contained its own amplification unit.

MR. W. J. PARKER, referring to Mr. Shallosky's suggested method for the polarographic determination of uranium, which would require a supporting electrolyte containing hydrofluoric acid, stated that although such a method was impracticable when a glass dropping-mercury electrode was used as cathode, it might well be that some of the new polarographic electrodes might permit the successful application of this promising method. It might be helpful to Mr. Shallosky if he mentioned that a considerable volume of work had been carried out both in America and in this country on the development of polarographic electrodes suitable for use in hydrofluoric acid media. Although some of these electrodes were based on principles other than that of the dropping-mercury electrode, nevertheless these electrodes might well have a special application to such methods as that suggested by Mr. Shallosky. References to some of these electrodes were to be found in papers by V. S. Griffiths and W. J. Parker (*Research*, 1954, 7, 546, and in *Anal. Chem. Acta*, 1956, 14, 194).

## Determination of Volatile Oil in Effluents

By J. G. SHERRATT

An account is given of a method for determining traces of neutral volatile oils, such as fuel oils, in waters and effluents. The solubility of certain types of fuel oil in water is considered, and some of the effects of pollution of natural waters by oil are briefly described.

THE determination of the glycerides of fatty acids and of mixed high-boiling hydrocarbon oils in effluents and river waters within limits of accuracy that are acceptable for most purposes does not present intrinsic difficulty, since these classes of compounds can usually be extracted by appropriate solvents, from which they can be recovered and ultimately weighed. For obvious reasons mixtures of volatile oils, such as occur in fuel oils and similar commercial products, cannot be determined in this way, nor can methods that depend upon the principle of distillation and subsequent volumetric measurement of the separated "oil" be made sufficiently sensitive to determine a few parts per million in effluents or river waters. Many

excellent methods based upon absorption spectrophotometry have been proposed for the determination of individual hydrocarbons, but these methods are invariably too specific to be of value to the water analyst for routine examinations for oil.

Despite the fact that the ever-increasing use of fuel oil has already created serious problems by polluting rivers, estuaries and, indeed, the oceans, very few methods have been published for determining traces of volatile oils. A method based upon gasometric measurement has been proposed by Webber and Burkes<sup>1</sup> for the determination of light hydrocarbons (including butadiene) in rubber-works waste waters, but its application is restricted, since many effluents and most river waters contain dissolved inert gases that would interfere. The danger of discharging relatively large quantities of volatile hydrocarbons into sewers is obvious, but it is not always appreciated that a few parts per million of commercial fuel oils may cause serious damage in rivers, not only by collecting behind weirs and on the surface of slow-flowing water and thereby interfering with atmospheric oxygen-exchange,<sup>2,3</sup> but also by their specific toxicity to fish<sup>3</sup> and their relatively high biochemical oxygen demand (B.O.D.). For example, during some recent tests in this laboratory, it was found that the addition of two drops of either petrol, white spirit or kerosene (paraffin burning oil) to 1 litre of a fairly clean river water raised the B.O.D. from 3.5 to over 10 p.p.m. The effect was not dependent upon "seeding" the water with extraneous bacteria.

Clearly there is a need for a widely applicable method of analysis that will detect and determine neutral volatile oils in the range of 5 to 500 p.p.m. in any kind of water (sewage, effluents and river waters). For practical purposes extreme accuracy is rarely essential, but the method should be capable of demonstrating increments of about 2 to 3 mg per litre in the lower range and 20 to 30 mg per litre in the higher.

#### EXPERIMENTAL

The heterogeneous character of commercial fuel oils and the extreme stability of aliphatic hydrocarbons militate against methods of analysis based upon chemical reaction. Of the physical properties, specific-gravity and refractive-index measurements are impracticable in the lower ranges of concentration, and spectrophotometric absorption is too specialised to form the basis of a general method. Most commercial oils fluoresce under ultra-violet excitation, but an attempt to utilise this effect soon indicated that it was too variable and too subject to extraneous influence to be of value for general quantitative use.

Among the properties characteristic of volatile oils is their miscibility with acetone and their relative insolubility in water. If a dilute solution of oil in acetone is mixed with an excess of water, the oil is thrown out of the solution in the form of a white turbidity; under suitable conditions the turbidity may be made proportional to the quantity of oil and the effect used to determine commercial oil dissolved in acetone. If the dilution in acetone is made with water containing a trace of synthetic detergent, the emulsion is stable for many hours and if, in addition, the water is acid, basic substances will not usually interfere. Trials of the sensitivity of the effect showed that as little as 0.001 ml of kerosene or white spirit, dispersed in 50 ml of liquid, give a faint but perceptible turbidity and additional increments of the same order could easily be distinguished from one another. With commercial petrol and the lower-boiling hydrocarbons the limit for detection was about 0.003 to 0.004 ml at this dilution, but if the final volume was reduced to 10 ml instead of 50, 0.001 ml of petrol was just perceptible by careful comparison with a blank and 0.002 ml was unmistakable.

Before this method of determination of volatile oils could be applied to effluents or natural waters, a method of separating and concentrating the oils had to be devised. Since extraction with organic solvents cannot be used, some form of selective adsorption appeared to offer the most readily available means. After a number of trials activated carbon was selected as being a suitable absorbent, and a brand kindly supplied by Messrs. Sutcliffe, Speakman & Co. Ltd., of Leigh, Lancs., was used for the purposes described in this paper. One gram of the carbon was supported on a plug of glass-wool in a small cylindrical funnel and 0.04 ml of kerosene was measured from a micro-burette on to it. Then 50 ml of water were passed through the carbon and allowed to drain away, excess of water finally being removed by gentle blowing. Five successive 1-ml volumes of acetone were passed through the carbon and collected in a graduated measuring cylinder. The last few drops of acetone were displaced from the carbon by blowing through the funnel. The acetone was diluted to exactly 50 ml with a solution containing 1 ml of sulphuric acid and 1 ml of Teepol per litre.

The resultant turbidity was compared with a standard containing 0.04 ml of kerosene dissolved in 5 ml of acetone and diluted to 50 ml with the Teepol solution. There was no visible difference between the turbidity in the two tubes and the amount of light absorbed or dispersed by both liquids, measured in a 1-cm cell in a photometer at 5500 Å, was practically identical.

This experiment indicated that traces of oil adsorbed on activated carbon could be recovered quantitatively by extracting it with acetone, but when 0.04 ml of oil was shaken with 1 litre of water and the whole of the liquid filtered through the carbon, only 30 to 40 per cent. of the quantity added could be recovered. The loss was not due to oil being left in the original vessel, which was washed out with acetone after all the water had been filtered. Several attempts were made to improve the percentage recovery by steam-distilling the oil in an apparatus arranged so that the condensed liquid passed through the carbon before reaching the free atmosphere. By replacing the carbon filters successively after increments of 50 ml of water had been distilled and finally extracting each filter with acetone and testing the extracts in the manner already described, it was found that no more oil could be recovered on carbon after 250 ml of water had passed over from an original volume of 1 litre of water and 0.05 ml of kerosene. It was also proved, by stopping the inflow of steam, continuing the distillation almost to dryness, filtering the remaining aqueous liquid through carbon and subsequently extracting the flask and the carbon with acetone, that no oil remained unvolatilised. Nevertheless, in a series of experiments, the average quantity of kerosene recovered varied between 40 and 50 per cent. of the quantity originally added to the distillation flask. Rather better percentage recoveries were obtained if the experimental oil was petrol, all of which was found to pass from the distillation flask in the first 100 ml. During the course of these trials it was noticed that the percentage of oil recovered varied inversely with the quantity of water distilled, which suggested that some of the oil was re-extracted from the carbon by water. This theory was confirmed by adsorbing measured volumes of volatile oil on carbon and washing it with various quantities of water before extracting the carbon with acetone and measuring the turbidity of the oil - water dispersion. In every instance, loss of oil increased proportionately with the volume of water that was filtered through the carbon. The loss was not appreciably diminished by first cooling the washing water to approximately 3° C.

In view of this hitherto unsuspected solubility factor, it became apparent that quantitative recovery of small amounts of volatile oil would not be obtained by filtering aqueous liquids through carbon, with or without intermediate distillation. Attempts were made, therefore, to volatilise the oil in a current of air. This procedure was much more successful in recovering the oil and so the method that follows was finally adopted.

## METHOD

### APPARATUS—

*A small cylindrical or thistle funnel* with a stem about 18 to 20 cm long and 0.5 cm in diameter. The stem is fitted with a rubber stopper that will fit tightly into the upper end of a reflux condenser.

*A 2-necked flask* (the "sulphur dioxide" flask of Monier-Williams) of about 1.5 litres capacity, fitted with a reflux condenser in one neck and with an air-delivery tube, reaching to the bottom of the flask, in the other.

*A small aquarium aerator*, or other means of directing air through the apparatus.

*Test tubes* (6 inch  $\times$   $\frac{1}{8}$  inch), graduated at 2 ml and 10 ml.

### REAGENTS—

*Acid Teepol*—A distilled water solution containing 1 ml of concentrated sulphuric acid and 1 ml of Teepol per litre. Cool to between 5° and 10° C before use.

*Activated carbon*—Obtainable from Messrs. Sutcliff, Speakman & Co. Ltd., Leigh, Lancs., quality No. 207, type B, mesh 20 to 40 B.S.S.

*Sodium hydroxide solution*—A 10 per cent. w/v solution of the analytical-reagent grade material in distilled water.

*Acetone*—Analytical-reagent grade.

### PROCEDURE FOR DETERMINING VOLATILE OIL IN THE RANGE 3 TO 15 mg PER LITRE—

Weigh 0.2 g of activated carbon and pack it lightly between tight plugs of glass-wool in the narrow stem of the small funnel (absorption tube). Arrange the flask and condenser

for reflux distillation in a current of air and fit the absorption tube into the outlet end of the apparatus (Fig. 1).

Samples of effluent or river water in which oils are to be determined should be collected with precautions to ensure that they are representative and should be contained in wide-necked bottles of clear glass, holding approximately 1 litre.\* Mark the level of the liquid on the outside of the bottle, for subsequent determination of the volume, and pour all the sample into the distillation flask. Rinse out the bottle with two portions of 2.5 ml of acetone,

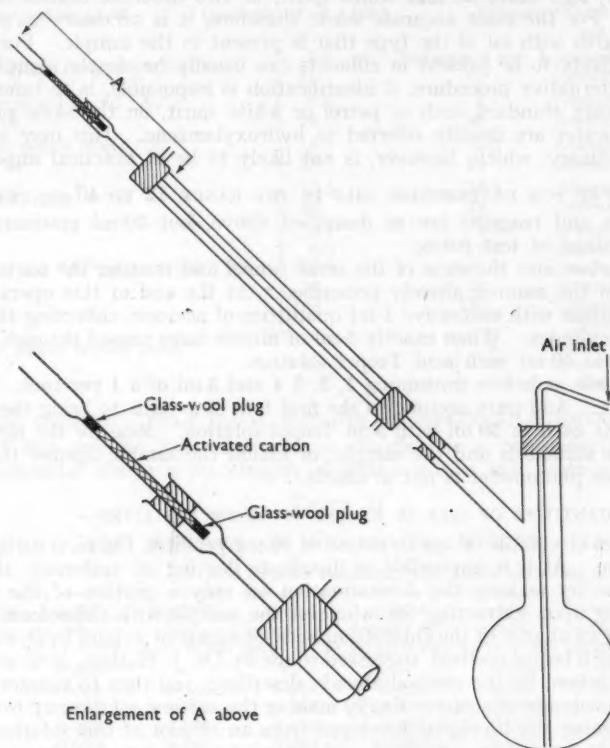


Fig. 1. Adsorption apparatus

taking care that the acetone dissolves any traces of oil left adhering to the inside of the sample bottle; pour the acetone into the distillation flask. Add sodium hydroxide solution to raise the pH of the sample to approximately 10. Connect the gas-delivery tube to the flask and pass a current of air through the sample, at such a rate that the bubbles can just be counted; gently boil the liquid. About 10 minutes after drops of acetone can no longer be observed forming in the condenser, discontinue heating the flask and remove the small funnel containing the carbon. Wash the carbon with acetone, added drop by drop, and collect the filtrate in a graduated test tube. When exactly 2 ml of acetone have been collected, dilute the filtrate to 10 ml with the acid Teepol solution.

#### PROCEDURE FOR PREPARING STANDARDS—

Prepare a solution containing 1.00 ml of petrol, sp.gr. 0.73, or other volatile oil (see note below), dissolved in and made up with acetone to 100 ml. From a micro-burette measure into a series of matched test tubes 0.4, 0.8, 1.2, 1.6 and 2.0 ml of this solution and

\* Sampling of liquids that contain visible floating oil requires specialised equipment and technique. A method is recommended by the A.B.C.M. - S.A.C. Joint Committee on Methods for the Analysis of Trade Effluents (*Analyst*, 1956, 81, 492).

dilute the first four of these to exactly 2 ml with acetone. Finally make each of the standards up to 10 ml with acid Teepol solution and match the sample visually against these standards.

NOTE—

It is shown subsequently (Table II) that equal weights (or volumes) of different classes of commercial fuel oils do not give the same degrees of turbidity when subjected to the above procedure, but that the variations between different oils of roughly the same category, *e.g.*, kerosene and white spirit, or two different brands of petrol, are insignificant. For the most accurate work, therefore, it is necessary to prepare comparison standards with oil of the type that is present in the sample. Fortunately the classes of oil likely to be present in effluents can usually be closely identified by their odour. An alternative procedure, if identification is impossible, is to refer the sample to some arbitrary standard such as petrol or white spirit, on the same principle that "phenols" in water are usually referred to hydroxybenzene. This may lead to some sacrifice of accuracy, which, however, is not likely to be of practical importance.

MODIFIED PROCEDURE FOR DETERMINING OILS IN THE RANGE 12 TO 40 mg PER LITRE—

The apparatus and reagents are as described above, but 50-ml graduated cylinders should be used instead of test tubes.

Pack 1 g of carbon into the stem of the small funnel and transfer the oil to the carbon by volatilising it in the manner already prescribed. At the end of this operation extract the oil from the carbon with successive 1-ml quantities of acetone, collecting the filtrate in a 50-ml graduated cylinder. When exactly 5 ml of filtrate have passed through the carbon, dilute the acetone to 50 ml with acid Teepol solution.

Prepare standards as before containing 1, 2, 3 4 and 5 ml of a 1 per cent. v/v solution of the oil in acetone. Add pure acetone to the first four standards to bring the volumes to 5 ml and then dilute each to 50 ml with acid Teepol solution. Measure the light absorbed or dispersed by the standards and the sample, or match the sample against the standards visually if a suitable photometer is not available.

PROCEDURE FOR QUANTITIES OF OILS IN EXCESS OF 40 mg PER LITRE—

If the quantities of volatile oil are in excess of 40 mg per litre, the final turbidity will be too deep to measure. As it is impossible to distribute floating oil uniformly, the difficulty cannot be overcome by making the determination on only a portion of the sample. A procedure depending upon extracting the whole of the sample with chloroform and subsequently hydrolysing an aliquot of the chloroform with an excess of sodium hydroxide was first developed, but a much better method, suggested to me by Dr. J. Haslam, is to adsorb all the volatile oil on the carbon, by the method already described, and then to extract the carbon with repeated small volumes of acetone, finally making the acetone solution up to a measured volume and determining the turbidity developed from an aliquot of this solution.

The above methods may be combined with an extraction procedure to determine the total oil in effluents and similar samples that may contain lubricating oil or diesel fuel of relatively high boiling point. Under the conditions prescribed only about 20 to 30 per cent. of diesel fuel, with an initial boiling point of about 180° C., is recovered on the carbon, the balance remaining in the flask. After all the volatile oil has been removed the liquid remaining in the flask is cooled, acidified with acetic acid or hydrochloric acid and extracted twice with light petroleum. The light petroleum extracts are combined, washed with a little water and shaken with 2 g of anhydrous sodium sulphate. The light petroleum is then filtered and transferred to a weighed flask. The solvent is evaporated and the residue dried and weighed. Subsequently it is dissolved in neutral alcohol and any acid is determined by titration with 0.02 N sodium hydroxide, phenolphthalein being used as indicator. In this way neutral volatile oil, non-volatile oil and fatty acid, free or combined with inorganic ions, *e.g.*, as soap, may be determined separately in one sample.

RESULTS

RECOVERY OF KNOWN QUANTITIES OF DIFFERENT FUEL OILS—

In Table I are given some of the results obtained by the above procedure when known quantities of different commercial volatile oils were added to 1 litre of water. In each case the final turbidity was matched against standards prepared from the oil under examination.

As it is impossible to measure very small quantities of volatile oil accurately and is inconvenient to weigh them, a 1 per cent. solution of oil in propylene glycol\* was used to measure the added oil in the range 0 to 30 mg. Quantities in excess of 30 mg were measured directly from a micro-burette.

TABLE I  
RECOVERY OF FUEL OILS

Description of oil	Quantity of oil added, mg	Quantity of oil recovered, mg
Cigarette lighter fuel, sp.gr. 0.70	{ 3.5 21	between 3 and 4 (visual) 19 (instrument)
First-grade petrol brand "A," sp.gr. 0.73	{ 4.4 36	4 (visual) 30 (instrument)
Commercial petrol brand "B," sp.gr. 0.73	{ 3.7 25	3.5 (visual) 21 (instrument)
White spirit, sp.gr. 0.785	{ 15.5 39	17.3 (instrument) 34 (instrument)
	{ 3.1 6.3	2.3 (visual) 5.5 (visual)
Kerosene brand "A," sp.gr. 0.785	{ 15.5 31 160	12 (instrument) 29 (instrument) 130 (visual, after chloroform extraction)
Diesel fuel, initial boiling point 180°C .. ..	10	{ 3 6 volatile non-volatile by extrac- tion and weighing

#### VARIATION OF TURBIDITY WITH EQUAL WEIGHTS OF DIFFERENT COMMERCIAL OILS—

Table II sets out the light dispersed or absorbed in a photo-electric photometer by different commercial oils at a wavelength of 5500 Å with a light path of 17 mm.

TABLE II  
LIGHT DISPERSED OR ABSORBED BY DIFFERENT OILS

Volume of oil dispersed in 50 ml of acid Teeopol solution, ml	Photometer readings, logarithmic scale, for						
	light petroleum, sp.gr. 0.646	lighter fuel, sp.gr. 0.705	petrol brand "A," sp.gr. 0.730	petrol brand "B," sp.gr. 0.730	white spirit, sp.gr. 0.785	kerosene brand "A," sp.gr. 0.785	kerosene brand "B," sp.gr. 0.785
0.005	0.005	—	—	—	0.068	0.095	0.100
0.010	0.015	0.032	0.021	0.025	0.168	0.166	0.165
0.020	0.050	0.095	0.069	0.060	0.318	0.336	0.338
0.030	0.066	0.176	0.185	0.180	0.545	0.565	0.560
0.040	0.095	0.290	0.280	0.285	0.662	0.660	0.650
0.050	—	0.390	0.450	0.430	—	—	—

It may be noted that the turbidity, as measured by light interference, usually increases with the specific gravity of the oil and, hence, with the proportion of hydrocarbons of higher molecular weight. This may be due to the dual effect of differences in refractivity and solubility. Very volatile hydrocarbons, such as light petroleum, are not likely to be met in practice and, although measurement made against arbitrary standards prepared, for example, from petrol or kerosene will impair the accuracy of the method if the oil in the sample is of a markedly different grade, it will probably be convenient to use them for routine examinations.

#### INTERFERING SUBSTANCES

The term "oil" lacks precision and any method of general application for the determination of oil cannot be specific. The qualifications "volatile" and "neutral" are useful in implying some restriction on the classes of compounds that are to be determined, and the method is designed not to include as "oil" certain volatile substances, *e.g.*, phenols, that are not usually so described. Clearly this method of determination will include substances that, under the conditions of the test, are volatile, neutral, soluble in acetone and insoluble in water if, in addition, they are also adsorbed on activated carbon. As there may be differences

\* Acetone was used as a solvent for diesel fuel instead of propylene glycol.

of opinion as to whether, e.g., the inclusion of nitrobenzene or certain other synthetic organic compounds as "oil" is legitimate, it is difficult to decide what would constitute interference in the direction of over-estimation. This difficulty is not, of course, peculiar to the proposed method; it applies equally to the determination of non-volatile oils by extraction procedures and to distillation procedures involving measurement of separated oil. In theory, at least, the number of organic compounds that may be present in an industrial effluent is almost infinite: within practical limits, therefore, investigation of possible interference in the direction of over-estimation must be confined to those classes of compound that may be present in effluents such as sewage, leaving the rare and exceptional problem to be considered on its merits. Among non-oily substances that are frequently encountered in effluents are hydrogen sulphide and alkaline sulphides and polysulphides: sulphur may be produced from these compounds under the conditions of the test. Sulphur is volatile in steam, soluble in acetone and insoluble in water. *Prima facie*, therefore, sulphur and sulphide compounds might interfere with the method of analysis, but tests with sulphur and polysulphides have indicated that in concentrations up to 1000 mg per litre these substances do not interfere.

On the negative side no substance has been encountered that leads directly to low results if the unavoidable limitations of a method that depends upon very low solubilities are taken into account. Clearly, compounds that are appreciably soluble in water, e.g., benzene, would tend to be under-estimated; and, although it would be easy to modify or adapt the principles involved to meet many specific problems, a detailed consideration of individual cases would be inappropriate in describing a method primarily designed to estimate volatile oils. In the sphere of river pollution, volatile oils are usually aliphatic hydrocarbons of low solubility.

In the presence of volatile-oil solvents, such as ketones, the procedure of transferring the oil from the sample to the carbon was found to take longer than usual, presumably because the reflux effect permits traces of the oil to be dissolved in the condensing liquid and returned to the flask. By continuing the passage of air until drops of condensing organic solvents were no longer visible in the condenser, satisfactory recovery of traces of oil in the presence of up to 2000 mg of acetone per litre was obtained.

#### SOLUBILITY IN WATER OF SOME COMMERCIAL OILS—

The method has been used to determine the solubility in water of some commercial fuel oils. An excess of the test oil was shaken with tap water in a shaking machine for 30 minutes and then allowed to settle in a separating funnel overnight. The aqueous layer was withdrawn and filtered through a wet No. 31 Whatman filter-paper. The filtrate was examined for volatile oil by the method described; the following results were obtained—

		Solubility, mg per litre
First-grade petrol brand "A"	..	23
Commercial petrol brand "B"	..	17
White spirit	..	17
Kerosene	..	3
Kerosene (repeat)	..	3

TABLE III  
VOLATILE OIL FOUND IN WATER SAMPLES

Sample number	Description of sample	Volatile oil, mg per litre (expressed as kerosene)	Remarks
1	River water from highly industrialised district	5.0	Known to contain surface drainage
2	As No. 1, after coagulation, settlement and filtration	0.0	—
3	Crude sewage from large military aerodrome	8.0	—
4	As No. 3, after treatment	0.0	—
5	Clean water from upland river	0.0	B.O.D. 1 p.p.m.
6	As No. 5, after receiving heavy pollution from organic chemical works	0.0	B.O.D. 10 p.p.m.
7	Crude sewage from rural area	0.0	Dry weather
8	As No. 7, after treatment	0.0	Dry weather
9	Drainage from open-cast coal mining, sample A	0.0	Contained 10 p.p.m. of non-volatile oil
10	Drainage from open-cast coal mining, sample B	6.0	Visible traces of oil and smell of diesel fuel

Table III shows some of the results that have been obtained on certain samples sent in for routine analysis, including samples of crude and treated sewage and of river waters that might be expected to contain traces of volatile oils derived from gas-works effluents and the surface drainage of industrial districts.

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## The Determination of Selenium in Effluents

BY D. N. FOGG AND N. T. WILKINSON

The American Public Health Association method for the determination of selenium has been investigated and found unsatisfactory, because the colour of the turbidity produced by the precipitated selenium differs in the sample solution and in the standards.

In the proposed method the selenium is first separated by distillation with hydrobromic acid and bromine in the presence of sulphuric acid. The selenium is then precipitated with ascorbic acid as a turbidity under standard conditions of acidity in both the sample and standard distillates. Under the conditions of the test reproducible colours and accurate results are obtained.

In the presence of organic matter full recovery of selenium is not attained when a wet destruction of the organic matter is carried out with nitric and sulphuric acids. Recovery is complete, however, if in addition to the nitric and sulphuric acids a small volume of perchloric acid is added.

THE method for the determination of selenium described by the American Public Health Association<sup>1</sup> is stated to be tentative, since it is conceded that the method gives low results.

We have examined the method and consider it to be unsatisfactory, because the same conditions are not maintained for both the preparation of the standard colours and the sample under test. These different conditions cause the colour turbidities to vary in tint from yellow to pink.

From the results of our experimental work we have developed a method requiring standard conditions and we have replaced the two reducing agents used in the A.P.H.A. method—sulphur dioxide and hydroxylamine—by one reducing agent, ascorbic acid.<sup>2</sup> This reagent reduces both the excess of bromine and precipitates the selenium consistently in a pink colloidal form, which permits easy matching of the sample solution with standards.

In the destruction of any organic matter by wet digestion with nitric and sulphuric acids, loss of selenium occurs. If, however, the digestion is done in the presence of a small amount of perchloric acid, complete recovery of selenium is obtained.

#### EXPERIMENTAL

Our first experiments were directed to ascertaining the accuracy of the A.P.H.A.<sup>1</sup> method.

A 5-ml portion of a standard selenium solution (1 ml = 0.00010 g of selenium) was added to 100 ml of distilled water and the selenium was determined by the procedure described by the A.P.H.A. Comparison of the test solution was made against a series of standards prepared from a standard distillate as described by the A.P.H.A. The colour of the turbidity produced in the test solution was yellowish pink, but in each of the standard solutions it was reddish pink, which made accurate matching impossible. It should be noted that the standards are prepared by first precipitating the whole of the selenium in the standard distillate and then diluting aliquots of the latter.

The experiment described above was repeated, but this time the standard distillate was diluted to 100 ml in a calibrated flask. Aliquots of the solution, e.g., 1.0, 2.5, 5.0, 7.5

and 10.0 ml, were placed into a series of 100-ml Nessler cylinders and each solution was diluted to 75 ml with distilled water. Each solution was then treated with sulphur dioxide and hydroxylamine hydrochloride as described by the A.P.H.A. No precipitate of selenium was obtained in any of the standards during the 1-hour standing time.

The result of this experiment appeared to indicate that the acidity of the solution is of importance when the reduction is carried out with sulphur dioxide and hydroxylamine.

EFFECT OF ACIDITY ON THE PRECIPITATION OF SELENIUM WITH SULPHUR DIOXIDE AND HYDROXYLAMINE—

A 2.0-ml portion of the standard selenium solution was added to each of five Nessler cylinders (100 ml capacity). Volumes of hydrobromic acid, *viz.*, 10, 20, 30, 40 and 50 ml, were added to each of the cylinders and the solutions were diluted to 75 ml with distilled water. Sulphur dioxide gas was passed into each solution for 5 seconds, and 2 ml of 10 per cent. hydroxylamine hydrochloride and then 1.0 ml of 5 per cent. gum arabic solution were added. Each solution was mixed and set aside for 1 hour. The results are shown in Table I.

TABLE I  
EFFECT OF ACIDITY ON SELENIUM PRECIPITATION

Volume of hydrobromic acid in test solution, ml	Result
10	No turbidity
20	Trace of turbidity
30	Partial development of turbidity
40	Full development of turbidity*
50	Full development of turbidity*

\* The turbidities produced in solutions to which 40 ml and 50 ml of hydrobromic acid had been added were alike in colour and intensity, and were therefore regarded as having "full development of turbidity."

The result of this experiment shows that it is necessary to have present a minimum of 40 ml of 48 per cent. hydrobromic acid in a volume of 78 ml in order to obtain complete precipitation of the selenium.

Many experiments were carried out in an endeavour to standardise the conditions of the test with sulphur dioxide and hydroxylamine hydrochloride as reducing agents so that the same shade of turbidity was reproducible.

PRECIPITATION OF SELENIUM BY SULPHUR DIOXIDE AND HYDROXYLAMINE IN SIX IDENTICAL SOLUTIONS—

Six identical solutions were prepared in 50-ml Nessler cylinders, each containing 20 ml of hydrobromic acid, 5 ml of hydrobromic acid - bromine reagent, 2.5 ml of the standard selenium solution and 10 ml of distilled water. The reagents added to each cylinder were of the same quality and taken from the same bottles.

Sulphur dioxide gas was passed into each solution until the bromine was reduced and for 5 seconds longer, and then 2 ml of 10 per cent. w/v hydroxylamine hydrochloride solution and 1.0 ml of 5 per cent. w/v gum arabic solution were added. The solutions were mixed and set aside for 1 hour. As far as could be judged, the reduction with sulphur dioxide was carried out in the same manner for each solution. A reddish-pink turbidity was produced in each of three solutions, a yellowish-pink turbidity was produced in each of two solutions and an intermediate tint of pink and yellow turbidity was produced in the remaining solution.

In view of the difficulty of standardising the conditions for the precipitation of selenium with sulphur dioxide, experiments were next carried out with ascorbic acid<sup>2</sup> as reducing agent.

PRECIPITATION OF SELENIUM WITH ASCORBIC ACID IN SIX IDENTICAL SOLUTIONS—

Six identical solutions were prepared in 50-ml Nessler cylinders, each containing 20 ml of hydrobromic acid, 5 ml of hydrobromic acid - bromine reagent, 2.5 ml of the standard selenium solution and 10 ml of distilled water. The reduction was carried out by the addition of 0.4 g of ascorbic acid to each solution, the solution being mixed until the ascorbic acid had dissolved. On standing for 20 minutes and for at least 1 hour thereafter each solution produced coloured turbidities of the same intensity and tint.

## EFFECT OF ACIDITY ON THE PRECIPITATION OF SELENIUM WITH ASCORBIC ACID—

A 1.5-ml portion of the standard selenium solution was placed in each of six 50-ml Nessler cylinders. Different volumes of 48 per cent. redistilled hydrobromic acid were added (5 ml, 10 ml, 15 ml, 20 ml, 25 ml and 30 ml) and the solutions were diluted to 50 ml. Then 0.4 g of ascorbic acid was added and the solution was stirred until the ascorbic acid had completely dissolved. There was a full development of turbidity in each solution, as all the solutions were alike in the amounts of selenium precipitated. They were different however in that with increasing acidity the colour of the turbidity changed gradually from yellowish pink to almost pure pink.

The experiments were repeated with 0.5 ml of the standard selenium solution for each test, and similar results were obtained. It was decided to adopt ascorbic acid as the reagent for precipitating selenium.

## SEPARATION OF SELENIUM BY DISTILLATION—

Distillations of solutions containing known quantities of selenium were carried out, including the distillation of a "bulk" volume of standard selenium solution.

For the artificial sample solutions, 0.5, 2.0 and 2.5 ml of the standard selenium solution were each diluted to 25 ml with distilled water, and a distillation was carried out on each solution as follows.

To the 25 ml of solution contained in a 300-ml round-bottomed flask having a ground-glass socket 50 ml of hydrobromic acid and 6 ml of hydrobromic acid - bromine reagent were added. Then 25 ml of sulphuric acid, sp.gr. 1.84, were added carefully, the flask being cooled under running water during the addition. A small boiling rod was placed in the flask, and an adaptor and water-cooled condenser were fitted; the condenser had a long stem with narrow jet at the outlet. A 100-ml conical flask with a graduation mark etched at 80 ml was placed at the condenser outlet. Four millilitres of hydrobromic acid - bromine reagent were added to the conical flask, which was tilted so that the tip of the condenser outlet was below the level of the solution in the receiver. The contents of the distillation flask were heated, gently at first until air was displaced and afterwards more strongly, and the distillation was allowed to proceed until the volume of solution in the receiver was 80 ml. The conical flask was removed and the distillation was stopped. The distillate was transferred to a 100-ml calibrated flask, diluted to the mark with distilled water and the contents of the flask were mixed.

Distillation of 25 ml of the standard selenium solution was then carried out exactly as described above, and the distillate was also diluted to 100 ml with mixing.

A determination of the acidity of each sample distillate and the standard distillate was carried out as follows.

Five millilitres of each distillate were diluted with 100 ml of water and boiled until free from bromine. Each solution was cooled and titrated with *N* sodium hydroxide, with methyl orange as indicator. The acidity of each distillate was similar, 5 ml requiring 26.0 ml of *N* sodium hydroxide.

The concentration of the hydrobromic acid (48 per cent.) was also determined by titration with *N* sodium hydroxide and found to be 9 *N*.

Fifty millilitres of each artificial sample distillate were transferred to 50-ml Nessler cylinders. The acidity of the 50 ml of distillate in each of the Nessler cylinders was equivalent to  $260/9 \equiv 29$  ml of hydrobromic acid.

Suitable aliquots of the standard distillate were measured into 50-ml Nessler cylinders and sufficient hydrobromic acid was added so that the acidity of each standard solution was the same as that of 50 ml of the artificial sample distillate, *i.e.*,  $\equiv 260$  ml of *N* acid. Each standard was diluted to 50 ml with distilled water. Then 0.4 g of ascorbic acid was added to each standard and artificial sample solutions, each solution being mixed by stirring until the ascorbic acid had dissolved. Each solution was then set aside for 30 minutes. The turbidities produced in the sample solutions compared well in intensity and tint with the corresponding standard solutions containing the same amount of selenium, *i.e.*, 0.000025, 0.00010 and 0.000125 g of selenium.

A series of standards was also prepared from the standard selenium solution without distillation; 0.25, 1.0 and 1.25-ml portions of the standard selenium solution were measured into 50-ml Nessler cylinders, 29 ml of 48 per cent. hydrobromic acid were added to each and the solutions were diluted to 50 ml with distilled water. Reduction with ascorbic acid

was then carried out as described above. The turbidities produced were exactly comparable with the corresponding sample and standard distillate solutions described above.

Recovery of selenium was therefore quantitative by the distillation procedure and the various bromine contents of the distillates did not affect the subsequent reduction with ascorbic acid, provided that the sample and standard solutions both contained hydrobromic acid equivalent to 260 ml of *N* acid.

#### EFFECT OF ORGANIC MATTER—

*Destruction of organic matter with a mixture of nitric and sulphuric acids*—A 1.0-ml and a 2.5-ml portion of the standard selenium solution were placed in 250-ml beakers; each solution was diluted to 50 ml with distilled water and 0.2 g of Quebracho tannin was added. Then 5 ml of nitric acid, sp.gr. 1.42, were added and the solutions were evaporated to 10 ml, cooled and 5 ml of sulphuric acid were added to each. The solutions were evaporated on a sand-bath until white fumes of sulphur trioxide appeared. This treatment destroyed the organic matter. The solutions were cooled and 10 ml of distilled water were added to each, and the solutions were again evaporated until white fumes of sulphur trioxide appeared. The treatment with distilled water and evaporation was repeated once more.

Each solution was transferred to a distillation flask, 25 ml of distilled water being used for the transfer, and 50 ml of hydrobromic acid and 6 ml of hydrobromic acid - bromine reagent were added, and then 25 ml of sulphuric acid, sp.gr. 1.84, were added carefully, the flask being cooled under running water during the addition. The distillation of this solution was carried out as described previously and the distillate was diluted to 100 ml in a calibrated flask.

A standard distillate was prepared by distillation of 25 ml of standard selenium solution after addition of 50 ml of hydrobromic acid and so on, and the distillate was diluted to 100 ml in a calibrated flask.

Fifty millilitres or a smaller volume of the artificial sample distillates were transferred to 50-ml Nessler cylinders. Aliquots of the standard distillate were measured into similar Nessler cylinders. The acidity of the solutions was, when necessary, made equal to that of 50 ml of the sample distillate by adding hydrobromic acid and then diluting to 50 ml. The selenium was then precipitated by addition of 0.4 g of ascorbic acid to each. The results obtained by visual comparison are given in Table II.

TABLE II

#### EFFECT OF OXIDATION OF ORGANIC MATTER WITH NITRIC - SULPHURIC ACID ON SELENIUM RECOVERY

Volume of aliquot of sample distillate taken, ml	Selenium added in aliquot, g	Selenium found in aliquot, g
50	0.00005	0.000038
50	0.000125	0.00010
50	0.00005	0.000038
50	0.000125	0.000075
10	0.00020	0.00016
50	0.00020	0.00006

We thought that the low results might be due to the precipitation of selenium by nitrous acid formed during the wet-oxidation procedure. We therefore decided to carry out a treatment of selenium solution in the absence of organic matter with nitric and sulphuric acids and then carry out the test for selenium by the method described above. The results are given in Table III.

TABLE III

#### EFFECT OF TREATMENT WITH NITRIC - SULPHURIC ACID ON SELENIUM RECOVERY

Volume of aliquot of sample distillate taken, ml	Selenium added in aliquot, g	Selenium found in aliquot, g
50	0.000025	0.000025
50	0.00010	0.00010
50	0.000125	0.000125

These results supported our opinion that nitric acid was not a strong enough oxidising agent to prevent loss of selenium during a wet oxidation of organic matter with nitric and sulphuric acids.

Further confirmation of this was obtained in another experiment. After destruction of organic matter by wet digestion with nitric and sulphuric acids the nitric - sulphuric acid complex that forms in such a digestion was decomposed by addition of 10 ml of a saturated solution of ammonium oxalate and the solution was evaporated until white fumes of sulphur trioxide appeared. Elemental selenium was observed in the solution.

*Destruction of organic matter with a mixture of nitric, perchloric and sulphuric acids—* Experiments were carried out to ascertain what effect a small addition of perchloric acid would have in helping to prevent loss of selenium during destruction of organic matter by wet oxidation.

Different volumes of the standard selenium solution were placed in 250-ml beakers and each solution was diluted to 50 ml with distilled water and 0.2 g of Quebracho tannin was added to each. Then 5 ml of nitric acid, sp.gr. 1.42, and 1 ml of 60 per cent. perchloric acid were added to each solution, which was then evaporated to 10 ml. Each was cooled and 5 ml of sulphuric acid were added; the solutions were then evaporated on a sand-bath until white fumes of sulphur trioxide appeared. The solutions were cooled, 10 ml of distilled water were added to each, and they were evaporated until white fumes again appeared. The treatment with distilled water and evaporation was repeated once more.

Each solution was transferred to a distillation flask, 25 ml of distilled water being used for the transfer. From this point the procedure was exactly as described for the previous experiment. The results are given in Table IV.

TABLE IV

EFFECT OF OXIDATION OF ORGANIC MATTER WITH NITRIC - PERCHLORIC - SULPHURIC ACID ON SELENIUM RECOVERY

Volume of aliquot of sample distillate taken, ml	Selenium added in aliquot, g	Selenium found in aliquot, g
50	0.000025	0.000025
50	0.00010	0.00010
50	0.000125	0.000125
10	0.00020	0.00020
50	0.00002	0.00002

The method was then tried out on solutions each containing 0.003 g of calcium, 0.0008 g of magnesium, 0.005 g of sulphate, 0.002 g of chloride, 0.0002 g of tin, 0.00015 g of arsenic and 0.5 g of tannin in a volume of 50 ml.

Different volumes of the standard selenium solution containing 0.00025 g, 0.0025 g, 0.0020 g and 0.00004 g of selenium were added to four solutions of the above composition. A blank test was also performed.

The selenium in the solutions was then determined as described under "Method." The results are given in Table V.

TABLE V

EFFECT OF ADDED SUBSTANCES ON SELENIUM RECOVERY

Volume of aliquot of sample distillate taken, ml	Selenium added in aliquot, g	Selenium found in aliquot, g
50	nil	nil
50	0.000125	0.000125
10	0.00025	0.00025
10	0.00020	0.00020
50	0.00002	0.00002

The experiments were repeated in the presence of the following amounts of impurities in each test: 0.03 g of calcium, 0.01 g of magnesium, 0.05 g of sulphate, 0.02 g of chloride, 0.002 g of tin, 0.002 g of arsenic and 0.5 g of tannin in a volume of 50 ml.

Different volumes of the standard selenium solution containing 0.00002 g, 0.00010 g, 0.00060 g and 0.0025 g of selenium were added to four solutions of the above composition.

A blank test was also performed. The selenium in the solutions was then determined as described under "Method." The results are given in Table VI.

TABLE VI

## EFFECT OF ADDED SUBSTANCES ON SELENIUM RECOVERY

Volume of aliquot of sample distillate taken, ml	Selenium added in aliquot, g	Selenium found in aliquot, g
50	nil	nil
50	0.00001	0.00001
50	0.00005	0.00005
25	0.00015	0.00015
10	0.00025	0.00025

## METHOD

## REAGENTS—

*Nitric acid, sp.gr. 1.42.*

*Sulphuric acid, sp.gr. 1.84.*

*Perchloric acid, 60 per cent.*

*Methyl orange indicator solution.*

*Sodium hydroxide, 1-0 N.*

*Hydrobromic acid, redistilled*—Purify the acid by distillation. Collect the colourless middle fraction of the distillate. Determine the hydrogen bromide content of the collected fraction by titrating 5 ml with *N* sodium hydroxide, using methyl orange as indicator.

*Hydrobromic acid - bromine reagent*—Mix 3 ml of bromine with 197 ml of redistilled hydrobromic acid.

*Standard selenium solution*—(a) *Stock solution*: Weigh 1.405 g of selenium dioxide and dissolve it in distilled water. Transfer the solution to a 1-litre calibrated flask, add 80 ml of redistilled hydrobromic acid and dilute the solution to 1 litre. (b) *Dilute solution*: Measure 100 ml of the selenium stock solution into a 1-litre calibrated flask. Add 10 ml of redistilled hydrobromic acid and dilute the solution to 1 litre.

$$1 \text{ ml} \equiv 0.00010 \text{ g of selenium.}$$

*Ascorbic acid.*

## PROCEDURE FOR TREATING THE SAMPLE—

Measure a suitable volume of the sample into a beaker. Acidify the solution by the addition of nitric acid and add 5 ml in excess; then add 1.0 ml of 60 per cent. perchloric acid. Evaporate the sample to about 10 ml and then cool it. Add 5 ml of sulphuric acid and heat the solution on a sand-bath until white fumes appear. If the organic matter is not completely destroyed at this stage, add a further 1 ml of nitric acid and heat the solution again until white fumes appear. Allow the solution to cool, then add 10 ml of distilled water and heat the solution until white fumes appear. Repeat the treatment with distilled water and evaporate a second time.

## PROCEDURE FOR DISTILLING THE SELENIUM—

Cool the solution and transfer it to the distillation flask, using 25 ml of distilled water for the transfer. Add 50 ml of hydrobromic acid and 6 ml of the hydrobromic acid - bromine reagent. Then slowly and carefully add 25 ml of sulphuric acid to the contents of the flask, cooling the flask during the addition. Place a boiling rod inside the distillation flask. Fit an adaptor and water-cooled condenser to the flask and place a 100-ml conical flask, graduated at 80 ml and containing 4 ml of hydrobromic acid - bromine reagent, at the condenser outlet; tilt the conical flask so that the tip of the condenser lies below the level of the reagent.

Heat the contents of the distillation flask, gently at first until the solution is boiling and afterwards more strongly, and allow the distillation to proceed until the volume of solution in the receiver is 80 ml. Remove the receiver and discontinue the distillation. Transfer the distillate to a 100-ml calibrated flask, dilute the solution to the mark with distilled water and mix.

## PROCEDURE FOR PREPARING A STANDARD SELENIUM DISTILLATE—

Measure into a distillation flask similar to that used for the sample solution, 25 ml of the dilute selenium solution ( $1 \text{ ml} \equiv 0.00010 \text{ g of selenium}$ ) and follow the same procedure

for the distillation of selenium as described above, commencing with the addition of 50 ml of hydrobromic acid. Allow the distillation to proceed until the volume of solution in the receiver is 80 ml. Transfer the distillate to a 100-ml calibrated flask and dilute the solution to the mark with distilled water and mix.

#### PROCEDURE FOR COLORIMETRIC DETERMINATION—

Determine the acidity of the sample and standard distillate solutions on an aliquot of each solution as follows.

Measure 5 ml of the solution, add 100 ml of distilled water and boil the solution free from bromine, but not below 50 ml. Cool the solution, add 2 drops of methyl orange indicator and titrate with *N* sodium hydroxide.

Measure aliquots of the standard distillate solution covering the range 0 to 10 ml (*i.e.*, 0 to 0.00025 g of selenium) in steps of 1 ml into 50-ml Nessler cylinders. From the results of the above titrations add a calculated volume of hydrobromic acid to each cylinder so that the acid content of each standard is the same as that of 50 ml of sample distillate solution. Dilute each standard to 50 ml with distilled water.

Measure 50 ml of the sample distillate solution into a 50-ml Nessler cylinder. Precipitate the selenium in the sample and standard solutions by adding 0.4 g of ascorbic acid to each solution and stir the solutions until the ascorbic acid has dissolved. Set the solutions aside for 30 minutes, and then visually match the coloured turbidity in the sample solution against the coloured turbidities in the standard solutions.

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IMPERIAL CHEMICAL INDUSTRIES LIMITED  
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## The Polarographic Determination of Boron

BY D. T. LEWIS

No polarographic observations on boron derivatives are recorded in the literature and it is generally understood that the simple boric acids do not yield polarograms when electrolysed at the dropping-mercury electrode. It has been found that, in aqueous sulphite media and in presence of polyhydroxy derivatives, characteristic polarographic waves are produced if orthoboric acid is present in solution, concentrations of 0.0001 g of the acid per ml being readily discernable by this technique.

In interpreting this phenomenon, it has been established that the polarographic waves are in reality due to the liberation of free sulphurous acid by the action of the relatively strong polyhydroxyboric acid complex on the sulphite additive. The formation of such polarograms is, however, definite qualitative evidence for the existence of boric acid in solution.

ORTHOBORIC acid behaves in solution as a weak monobasic acid and dissociates according to the scheme—



the dissociation constant having the value of  $6.4 \times 10^{-10}$  at  $18^\circ\text{C}$ . Addition of polyhydroxy derivatives such as glycerol, galactose or mannitol to the boric acid solution results in the formation of a complex acid, *i.e.*, mannitoboric acid, which possesses a greatly increased degree of dissociation and is accurately titratable in the presence of phenolphthalein as indicator.

When subjected to examination by the polarographic method, neither orthoboric nor mannitoboric acid gives any indication of the development of a characteristic wave in the normal voltage range. In the presence of mannitoboric acid, however, addition of sodium

sulphite solution causes the immediate formation of two distinctive waves at half-wave potentials of  $-0.50$  and  $-1.01$  volts, respectively, with respect to the internal mercury anode. A typical polarogram thus obtained is shown in Fig. 1.

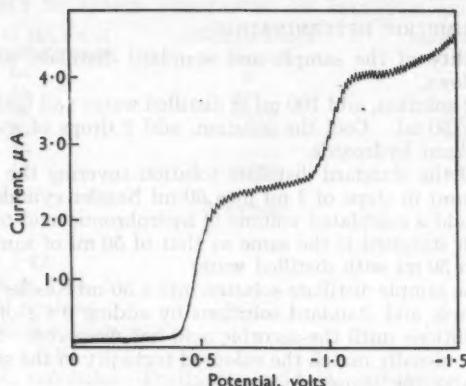


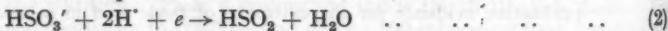
Fig. 1. Polarogram of boric acid in mannitol - sulphite

The application of the normal polarographic technique to the quantitative determination of a given compound depends essentially on the existence of a linear relation between the wave height as observed on the polarogram and the concentration of substance in the solution being examined. In the present instance the wave height certainly increased with increasing boric acid concentration, but the relationship between these two functions was not of a linear character. It soon became apparent that the observed waves, although dependent on the presence of boric acid in solution, were essentially the reduction curves of some other compound that was being produced by the addition of mannitol to a boric acid - sodium sulphite mixture. This reducible material could only be sodium bisulphite, produced directly by acidification of a sulphite base.

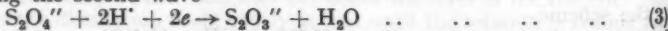
It was decided to examine this phenomenon in some detail, as it might afford a means whereby the polarograph could be applied to the qualitative and quantitative determination of boron.

The reduction of sulphur dioxide in acid solutions has been studied by Kolthoff and Miller,<sup>1</sup> who established that the diffusion current was directly proportional to the concentration of the gas in solution, the diffusion coefficient being  $2.04 \times 10^{-5}$  per sq. cm per second at  $25^\circ\text{C}$ . They found that only one polarographic wave existed in acid solutions ( $\text{pH} = 1$  to 4), but at  $\text{pH} 6$ , a second smaller wave was seen to develop, the half-wave potentials at this  $\text{pH}$  being  $-0.67$  and  $-1.23$  volts, respectively, against the saturated-calomel electrode. They concluded that no waves were produced in solutions in which the potential of the hydrogen ion exceeded 7. During the course of the present investigation, we have obtained excellent polarograms in sulphite solutions with  $\text{pH}$  values from 6.0 to 8.02.

Kolthoff and Miller postulated that in the more alkaline solutions the first wave represented direct reduction of the bisulphite ion in accordance with the scheme—



The  $\text{HSO}_2$  formed then polymerises to yield hyposulphurous acid, whose anion is further reduced as follows, giving the second wave—



The instability of hyposulphurous acid in strongly acidic media explains the formation of only one wave at low  $\text{pH}$  values.

#### EXPERIMENTAL

All the polarograms recorded during this investigation were obtained on the standard Cambridge polarographic instrument, temperature being controlled at  $25^\circ\text{C}$ . The mercury cathodes had a drop time of between 2 and 4 seconds and the galvanometer was generally employed at a sensitivity of 1/30 and a damping of 3 units. Calibration of the galvanometer

by Kolthoff's method gave an average value of  $4.92 \times 10^{-3} \mu\text{A}$  per scale division of the polarograms when the galvanometer was used at normal sensitivity.

The base solution employed consisted essentially of a solution that was  $M/5$  with respect to sodium sulphite and  $M/3$  with respect to mannitol. The presence of sulphite rendered unnecessary the normal routine of de-oxygenating the solutions with purified nitrogen, and polarograms were therefore recorded directly on the solutions prepared by admixture of this base solution with boric acid.

The experimental results in Table I are typical of a determination, wave heights being measured by a published method.<sup>2</sup> The values for wave heights given in the tables represent the heights of the first wave of the polarogram in terms of galvanometer readings at maximum sensitivity.

TABLE I  
EXPERIMENTAL RESULTS

Experiment 1—

Boric acid (10 g per litre), ml	$M/3$ mannitol + $M/5$ sodium sulphite, ml	Water, ml	Concentration of boric acid (c), moles per litre	Wave height (h)	$\frac{c}{h} \times 10^5$
10	15	0	0.06471	1650	3.92
8	15	2	0.05177	1200	4.31
6	15	4	0.03883	705	5.51
4	15	6	0.02588	300	8.63
3	15	7	0.01942	150	12.91
1.25	15	8.75	0.00809	30	26.97

The inconstancy of the Ilković  $c/h$  ratio is apparent. When experiment 1 was repeated with twice the concentration of mannitol in the base solution, the wave height was virtually unaffected. Replacement of the mannitol by an equal molar concentration of glycerol caused a marked diminution in the diffusion current and the half-wave potential moved from  $-0.5$  to  $-0.55$  volt with respect to the mercury anode.

TABLE II  
EXPERIMENTAL RESULTS

Experiment 2—

Boric acid (10 g per litre), ml	$M/3$ mannitol + $M/5$ sodium sulphite, ml	Water, ml	Concentration of boric acid, moles per litre	Wave height	pH	$h$
20	30	0	0.065	1650	6.84	21.3
15	30	5	0.048	900	7.04	21.3
10	30	10	0.033	435	7.26	21.3
5	30	15	0.016	101	7.60	21.1
2.5	30	17.5	0.008	30	8.02	21.2
0	30	20	0.000	0	9.38	—

Experiment 3—

0.1 N sodium baborate, ml	$M/3$ mannitol + $M/5$ sodium sulphite, ml	Water, ml	Concentration of sodium baborate, moles per litre	Wave height	pH	$h$
20	30	0	0.04	1500	7.25	21.3
15	30	5	0.03	1035	7.36	21.3
10	30	10	0.02	525	7.55	21.2
5	30	15	0.01	129	7.96	21.2
0	30	20	0.00	0	9.45	—

Experiment 4—

0.1429 M sodium bisulphite, ml	$M/3$ mannitol + $M/5$ sodium sulphite, ml	Water, ml	Concentration of sodium bisulphite, moles per litre	Wave height	pH	$h$
20	30	0	0.057	1290	7.0	21.5
15	30	5	0.043	780	7.2	21.5
10	30	10	0.028	360	7.4	21.5
5	30	15	0.014	90	7.8	21.5

Wave heights in glycerol solution are only about 1/15 of those observed in mannitoboric acid solutions of the same concentration. If the solution is made strongly alkaline with sodium hydroxide, the reduction waves completely disappear. It was, therefore apparent that measurements of pH should be taken simultaneously with the polarographic readings if a true picture of the phenomenon under study was to be secured. The results in Table II show the effect of mixing independently either the boric acid, sodium bisulphite or 0.1 N sodium baborate solution with the  $M/3$  mannitol -  $M/5$  sodium sulphite base solution, pH values being measured with the glass electrode. These three substances gave polarograms that were of generally similar character and possessed identical half-wave potentials.

In experiment 4, no boric acid was present and the polarographic curve represents the direct reduction of the bisulphite ion as indicated in equation (2), the concentration of this ion in moles per litre being given in the appropriate column.

Jellinek<sup>3</sup> states that the first dissociation constant of sulphurous acid has the value  $1.7 \times 10^{-2}$  at  $25^\circ C$ . Since we are studying the hydrolytic equilibrium (4), we are most concerned with the second dissociation constant for which the same author estimates the approximate value  $5 \times 10^{-6} = K_d$ . Kolthoff gives a value of  $K_d = 1 \times 10^{-7}$ . In any case it is apparent that  $HSO_3'$  is a much weaker acid than mannitoboric acid, which for convenience we can refer to as HB, but is far stronger than boric acid, which has  $K$  (dissoc.)  $= 6.4 \times 10^{-10}$ . On addition of mannitol to a borate - sulphite solution, the mannitoboric acid formed is immediately and almost wholly converted into the feebly dissociated bisulphite ion as shown in the following equation, this latter ion being then reduced at the dropping-mercury cathode in accordance with the scheme already detailed—



It is difficult to express numerically the equilibrium suggested by equation (4), because of lack of information about the degree of dissociation of sodium sulphite. In experiment 2 the sulphite was originally  $0.2 M$ , but has been diluted in the test solution to  $0.12 M$ . If we assume that the sodium salt is almost completely dissociated at this concentration, i.e.,  $(SO_3'') = 0.12$ , and that any mannitoboric acid is converted wholly to bisulphite, we have the numerical results in Table III.

TABLE III  
CALCULATIONS FROM EXPERIMENT 2

Molar concentration of bisulphite and of mannitoboric acid	Molar concentration of sulphite	pH	$-\log K_d$ (calculated)
0.000	0.12	9.38	—
0.008	0.112	8.02	7.13
0.016	0.104	7.64	7.17
0.033	0.087	7.26	7.16
0.048	0.072	7.04	7.14
0.065	0.055	6.84	7.19

$$\frac{[HSO_3'][B']}{[HB][SO_3'']} = K_1 \quad \frac{[H^'][B']}{[HB]} = K_2$$

$$\frac{[H^'][SO_3']}{[HSO_3']} = K_d = 1.4 \times 10^{-7} = \frac{K_2}{K_1}$$

The value of  $K_d$  thus calculated is in complete agreement with that of Kolthoff<sup>1</sup> and suggests that the conversion of the boric acid to bisulphite is complete in presence of mannitol.

In an attempt to employ the polarographic results for the quantitative determination of boron, a relation was sought between the concentration,  $c$ , the wave height,  $h$ , and the hydrogen-ion concentration of the solution. Kinetically, the reaction at the dropping-mercury electrode for the first polarogram wave may be expressed by the equation

$$-\frac{dx}{dt} = k_1 [HSO_3'][H^']^2 = k_1 c [H^']^2 \quad \dots \dots \dots \quad (5)$$

It has been found that all the polarograms may be most accurately represented by the relation—

$$h^2 = k c [H^']^2, \quad i.e., 2 \log h - \log c + 2 \text{pH} = k \quad \dots \dots \dots \quad (6)$$

The final columns of the results in Table II show how accurately this equation is obeyed. The constant,  $k$ , is unaffected by the mannitol concentration, but is increased by increasing concentration of sulphite in the base solution. This is most clearly shown by the results in Table IV for experiments carried out at 25°C on a different Cambridge polarograph.

TABLE IV  
EXPERIMENTAL RESULTS

## Experiment 5—

0.01617 M boric acid, ml	M/3 mannitol + 0.2 M sodium sulphite, ml	Water, ml	Concentration of boric acid, moles per litre	Wave height	pH	$k$
20	30	0	0.06068	6000	6.84	22.4
15	30	5	0.04851	3550	6.98	22.4
10	30	10	0.03034	1700	7.24	22.5
5	30	15	0.01517	425	7.62	22.3
2.5	30	17.5	0.00759	150	7.96	22.4
0	30	20	0.0000	0	9.40	—

## Experiment 6—

0.01617 M boric acid, ml	M/3 mannitol + 0.4 M sodium sulphite, ml	Water, ml	Concentration of boric acid, moles per litre	Wave height	pH	$k$
20	30	0	0.06068	5175	7.24	23.1
15	30	5	0.04851	4350	7.25	23.1
10	30	10	0.03034	2000	7.44	23.0
5	30	15	0.01517	525	7.90	23.0
2.5	30	17.5	0.00759	150	8.04	22.6
0	30	20	0.0000	—	9.80	—

## Experiment 7—

0.01617 M boric acid, ml	Mannitol + 1.0 M sodium sulphite, ml	Water, ml	Concentration of boric acid, moles per litre	Wave height	pH	$k$
20	30	0	0.06068	4950	7.51	23.6
15	30	5	0.04851	4050	7.58	23.7
10	30	10	0.03034	1800	7.86	23.7
5	30	15	0.01517	360	8.25	23.4
2.5	30	17.5	0.00759	65	8.57	22.9
0	30	20	0.0000	0	10.3	—

The increase in the  $k$  value with sulphite concentration is apparent from the results in Table IV and for quantitative work a fixed mannitol-sulphite base must be consistently used. For general work, the 0.2 M concentration is recommended, as the wave height for a given concentration of boric acid decreases with increasing sulphite concentration and initial increasing pH of the base solution. Accepting the equation  $\log h^2 = \log c + 2 \text{ pH} = k$ , we can consider the case when  $h = 1$  ( $\log h = 0$ ). For this wave height we can accept the pH value of the base solution when the added boric acid is nil, i.e., pH = 9.4 for experiment 5. If we accept the value  $K_d = 1.4 \times 10^{-7}$  for the dissociation constant of the bisulphite ion, we would have at this pH a concentration of 0.00034 moles of  $\text{HSO}_3^-$  in the base solution, the  $\text{SO}_3^{2-}$  concentration being 0.12 M. With these values we calculate  $-\log c + 2 \text{ pH} = 22.3$ , which is almost exactly the result given for  $k$  in experiment 5. Similarly, the calculated values of  $k$  for experiments 6 and 7 are 23.1 and 23.6, respectively, which are in accord with those found experimentally. It thus appears that the relationship  $h^2 = k c [\text{H}^+]^2$  holds down to the limiting concentration of  $\text{HSO}_3^-$ , that is present in the base sulphite solution, and constitutes evidence that the mannitolboric acid is transformed completely into the undisassociated bisulphite ion, which is then reduced polarographically.

The qualitative and quantitative application of these results are obvious. A calibration graph may be drawn where the function  $\log h^2/[\text{H}^+]^2$  is plotted against  $\log c$ , and unknown concentrations of boric acid read directly from the graph.

Alternatively the function  $(\log h + \text{pH})$  may be plotted against  $\log c$  to give a series of parallel lines of slope 0.5 for sulphite base solutions of differing concentration.

In qualitative work, the boric acid may be freed from interfering substances by distillation as methyl borate, the alcohol is removed by boiling with potassium hydroxide, the pH is adjusted to neutrality and, after the addition of mannitol - sulphite, the presence of boric acid is confirmed polarographically by the appearance of two waves at the appropriate reduction potentials of the bisulphite ion. The sulphite employed should be polarographically free from bisulphite and a blank determination should be made simultaneously.

Alternatively, a standard boric acid solution may be employed and the unknown boric acid concentration determined by the method of standard addition, the increase in polarographic current being related to the unknown concentration of boric acid by the relationships previously described in this paper.

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## The Micro-determination of Chlorine in Small Samples of Polymerised and Copolymerised Vinyl Chloride

BY J. M. BATHER

The polymer is oxidised by a mixture of ceric ammonium sulphate and concentrated sulphuric acid in a closed system. The chlorine that is released then diffuses to a solution of ferrous ammonium sulphate, in which it is absorbed and reduced. The resultant chloride is then determined by the Volhard technique.

AN important group of textile finishing materials comprises the polymers of vinyl chloride, vinylidene chloride and their copolymers with vinyl acetate, vinyl alcohol and acrylonitrile. Since these polymers are unreactive chemically, differentiation is difficult, especially when only small amounts are available. Although their solubility in different organic solvents may give some clue to their identity, this is not very reliable and to make successive tests on small samples is not easy. However, it is sometimes possible to distinguish between these materials by means of their chlorine content, which serves, in many cases, to distinguish them from neoprene and rubber compounds containing chlorine. Characteristic values for a number of vinyl polymers and copolymers and for neoprene and two rubber compounds are given in Table I.

TABLE I  
CHLORINE CONTENTS OF SOME UNPLASTICISED COMMERCIAL POLYMERS

		Chlorine content, %
Poly(vinyl chloride)	..	57
Poly(vinylidene chloride)	..	73
Vinyl chloride - vinyl acetate copolymer 85/15	..	48
Vinyl chloride - acrylonitrile copolymer 60/40	..	33
Chlorinated polyethylene	..	65
Polychloroprene (neoprene)	..	40
Chlorinated rubber	..	64 to 66
Rubber hydrochloride	..	28 to 30

Some of these values are sufficiently widely separated to permit the use of a method that is not necessarily of the highest precision and that may be simplified when applied to these non-volatile materials. Fusion appeared to be the simplest method for obtaining the chlorine in an ionic form, but fusion with a mixture of sodium peroxide and sodium carbonate<sup>1</sup> proved unsatisfactory on a micro-scale.

Fusion with alkali metals<sup>2</sup> gave fair results with samples in powder form, but failed when the polymers were in the form of films. Wet oxidation was therefore applied in conjunction with a technique involving diffusion of the liberated chlorine. The technique adopted was a modification of the original diffusion process of Conway,<sup>3</sup> suggested by Katz, Abraham and Baker.<sup>4</sup>

#### EXPERIMENTAL

Preliminary experiments showed that the wet oxidation of poly(vinyl chloride) was likely to be too vigorous for the employment of the apparatus of Katz *et al.* Also, it was found undesirable to heat the absorbent solution owing to the probability of atmospheric oxidation (see below).

The reaction and absorption vessels, which were made of Pyrex glass, were therefore separated as shown in Fig. 1. The oxidation vessel, A, is connected by a greased ground joint to the cylindrical absorption flask, B, and secured by means of small springs attached to the lugs. The flask, B, is flattened on its lower surface in order to expose a larger surface of the absorbent solution.

Since reaction does not proceed in the cold, the reactants were heated by inserting vessel A into a hole in a copper block suspended above a bunsen burner and surrounded by an asbestos chimney as shown in Fig. 2. The chimney was needed to maintain the temperature, and to screen the absorption vessel from the source of heat.

To select a suitable absorbent, various quantities of powdered poly(vinyl chloride) were heated with an excess of oxidising agent and the amount of chlorine absorbed was determined.

For the determination of chlorine in cotton materials by the Conway diffusion technique, Naylor<sup>5</sup> has recommended sodium arsenite as absorbent, an iodine solution being used to determine the excess. When this technique was employed in the present work, the titre of iodine solution was greater than that of the "blank."

This discrepancy was traced to sulphur dioxide formed by partial reduction of the sulphuric acid present (see below). Neutral ferrous ammonium sulphate appeared to function satisfactorily, recoveries in excess of 90 per cent. being quite readily obtained, when precautions were taken to avoid atmospheric oxidation. The absorbent solution was accordingly prepared in the absorption flask itself by dissolving the solid in the minimum quantity of water and protecting it from heat as already described.

The chlorine was determined as chloride by the Volhard method, the necessary ferric ion indicator being conveniently produced *in situ* from the residual ferrous ion by addition of nitric acid to the reagent.

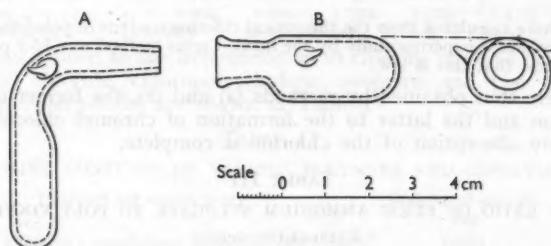


Fig. 1. Reaction and absorption vessels

As the results obtained with ferrous ammonium sulphate seemed satisfactory, this reagent was used in all the subsequent work.

#### OXIDISING AGENT—

A comparison of the following three oxidising agents was made by determining the recovery of chlorine from samples of pure unplasticised poly(vinyl chloride)—

- (a) concentrated sulphuric acid,
- (b) potassium dichromate and concentrated sulphuric acid, and
- (c) ceric ammonium sulphate and concentrated sulphuric acid.

The results are given in Table II; determinations in the absence of polymer have shown that these particular samples of reagents did not contain chlorine.

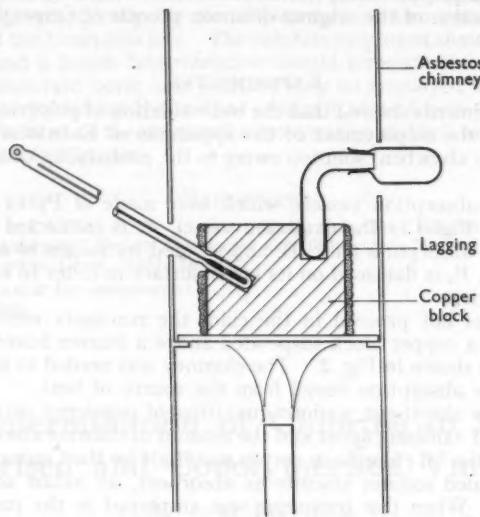


Fig. 2. Layout of apparatus

TABLE II

RECOVERY OF CHLORINE FROM POLY(VINYL CHLORIDE) ON OXIDATION

(a)	Concentrated sulphuric acid	Sample weight, mg	1.246	1.250	1.446	—	—	—	—
		Recovery, * %	81.0	81.0	85.0	—	—	—	—
(b)	Concentrated sulphuric acid and potassium dichromate	Sample weight, mg	1.286	1.403	1.592	—	—	—	—
		Recovery, * %	74.0	91.0	91.0	—	—	—	—
(c)	Concentrated sulphuric acid and ceric ammonium sulphate	Sample weight, mg	1.340	1.426	1.522	1.568	1.596	1.947	1.938
		Recovery, * %	99.5	100.5	99.0	99.5	99.5	99.5	100.1

\* The recoveries were calculated from the theoretical chlorine content of poly(vinyl chloride) (56.7 per cent.). The value determined experimentally by the micro-Carius method was 55.9 per cent., and there is some evidence to suggest that this is low.

Low results were thus obtained by methods (a) and (b), the former owing probably to incomplete oxidation and the latter to the formation of chromyl chloride, which oxidises the absorbent before absorption of the chlorine is complete.

TABLE III

VARIATION IN RATIO OF CERIC AMMONIUM SULPHATE TO POLY(VINYL CHLORIDE)

Sample weight, mg	Ratio of the weight of oxidant* to the weight of poly(vinyl chloride)	Recovery of chlorine, %
1.726	5	86.0
1.686	10	95.0
1.591	15	98.0
1.579	20	100.0
1.164	25	100.0
1.400	35	100.0
1.780	50	100.0
1.056	75	100.0
1.147	90	99.0
1.296	100	100.0

\* In addition to the amounts of ceric ammonium sulphate present, about 0.5 ml of concentrated sulphuric acid was added.

Since no reference to the formation of volatile ceric compounds under the conditions referred to above could be found in the literature, the behaviour of ceric ammonium sulphate as oxidant was investigated in more detail.

For the complete oxidation of poly(vinyl chloride), eleven equivalents of oxygen are required, corresponding to 111 g of hydrated ceric ammonium sulphate for 1 g of poly(vinyl chloride).

In order to determine whether the full amount was necessary in the presence of considerable amounts of concentrated sulphuric acid, a series of experiments was made in which the ratio of ceric ammonium sulphate to poly(vinyl chloride) was varied (see Table III). When the ratio is 20 or above, recovery of chlorine is evidently complete.

#### DURATION OF HEATING AND ABSORPTION—

Below 250° C the reaction was so slow that prolonged heating was necessary and the resulting expansion of air within the apparatus caused the seal to break, allowing the products of reaction to escape. Above 400° C the reaction tended to become so vigorous that contamination of the absorbent with the reactants was likely to occur by splashing. A temperature of 300° to 350° C was therefore chosen, and the effect on the recovery of chlorine by variation of the period of heating, within this range, is shown by the following results (the ratio of weight of oxidant to weight of poly(vinyl chloride) used in these experiments was 50)—

Weight of sample, mg	..	..	..	1.532	1.534	1.419	1.260
Heating period, seconds	..	..	..	20	40	60	80
Recovery of chlorine, %	..	..	..	66.5	99.0	99.0	100.0

In order to reduce the bulk of the reaction mixture, a ratio of ceric ammonium sulphate to poly(vinyl chloride) of about 50 was chosen, and with this amount of oxidant the recovery of chlorine was substantially complete after the mixture had been heated for 40 seconds.

Further experiments were carried out to ascertain the period required for complete absorption when the duration of heating was 50 seconds, the results being as follows—

Sample weight, mg	..	..	..	1.975	1.805	1.849	1.544
Absorption period, hours	..	..	..	0.5	1.0	2.0	3.0
Recovery of chlorine, %	..	..	..	71.0	84.0	99.0	99.0

In view of these results a period of 2.5 hours was allowed for this stage of the analysis.

#### APPLICATION OF THE METHOD—

Since samples of plastic recovered from solvent extracts of textiles are normally in the form of films, the method was tested with films prepared by dissolving the powdered poly(vinyl chloride) in tetrahydrofuran and evaporating the solution on a glass plate. The results were as follows—

Sample weight, mg	..	..	1.006	1.200	1.205	1.260	1.413	1.529	1.832
Recovery of chlorine, %	..	..	99.0	99.5	100.1	100.1	99.0	99.5	100.1

The method was applied to the determination of chlorine in three of the more common copolymers of vinyl chloride, chloropolyethylene, neoprene and two rubber compounds containing chlorine. The results are shown in Table IV.

TABLE IV  
CHLORINE CONTENTS OF VARIOUS POLYMERS AND COPOLYMERS

Polymer (or copolymer)		Weight of sample, mg	Chlorine found, %
Poly(vinyl chloride - vinylidene chloride) (66.7 per cent. of Cl <sup>†</sup> )	..	1.674 1.275	66.5
Poly(vinyl chloride - acetate) (48.9 per cent. of Cl <sup>†</sup> )	..	1.126 2.022	48.3 48.6
Poly(vinyl chloride - cyanide) (33.0 per cent. of Cl <sup>†</sup> )	..	1.438 1.374	33.0 33.0
Chloropolyethylene (65.0 per cent. of Cl <sup>†</sup> )	..	1.914 2.284	66.0 35.0
Neoprene (40.0 per cent. of Cl <sup>†</sup> )	..	2.200 2.013	35.0 35.0
Rubber hydrochloride (29.0 per cent. of Cl <sup>†</sup> )	..	1.265	29.0
Chlorinated rubber (65.0 per cent. of Cl <sup>†</sup> )	..	1.344	66.0

\* Determined by micro-Carius method.

† Nominal value.

As shown by the first four results in Table IV, the recovery of chlorine under the conditions employed is very close indeed to that obtained by the Carius method, and experiments on twenty-five samples of pure unplasticised poly(vinyl chloride) have yielded a standard deviation of  $\pm 0.21$  per cent. Low recoveries result, however, when the weight of the sample exceeds 2.5 mg. The concentration of oxidant, the period of heating and the time allowed for absorption have all been varied in attempts to explain this discrepancy but without success. It seems probable that it may be due to partial failure of the seal when the amount of carbon dioxide liberated is too large.

#### METHOD

It is important that the reagents used for the oxidation and absorption should not contain chlorine.

Weigh about 1.5 mg of the polymer into the reaction tube and cover it with 75 mg of powdered ceric ammonium sulphate. Add 0.5 ml of concentrated sulphuric acid, and mix thoroughly.

Dissolve 0.1 g of neutral ferrous ammonium sulphate in 1.0 ml of distilled water contained in the absorption flask and attach the flask to the reaction tube, the cone of which has been lightly greased with white petroleum jelly. Insert the reaction tube into a hole in the copper block, which is maintained at about 350° C., and after 50 seconds, remove the apparatus, and allow it to cool for 2.5 hours in such a position that the absorption flask remains horizontal.

Detach the absorption flask and rinse the inside of the cone of the reaction tube with distilled water, collecting the washings in the absorption flask. Add 0.02 ml of concentrated nitric acid to oxidise any remaining ferrous iron and 0.5 ml of 0.1 N silver nitrate to precipitate the chloride. After adding 0.25 ml of nitrobenzene,<sup>6</sup> titrate the excess of silver nitrate with 0.1 N potassium thiocyanate, using a microburette,<sup>7</sup> and agitating the solution with a magnetically operated stirrer. A blank solution is treated similarly, and the result is calculated from the difference between the two titres.

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THE BRITISH COTTON INDUSTRY RESEARCH ASSOCIATION

SHIRLEY INSTITUTE

DIDSBURY, MANCHESTER, 20

March 20th, 1956

## The Gravimetric Determination of Potassium in Sea Water As the Potassium Tetraphenylboron Salt

By K. F. SPOREK

A simple and rapid procedure for the gravimetric determination of potassium in sea water as the tetraphenylboron salt is described. The method requires no pretreatment of the sample before the determination, as under the conditions employed only potassium is precipitated.

In the analysis of sea water the determination of sodium and potassium, two of the important metallic ions, has always been a lengthy and tedious operation, and in a recently published review on the analysis of sea water Barnes<sup>1</sup> pointed out that the determination of potassium still presented a difficult problem to the analytical chemist. This is understandable when one considers the characteristics of the analytical methods that have been used, their sensitivity to interferences by certain metallic and non-metallic ions and the composition of sea water.

Since the introduction of sodium tetraphenylboron as a specific reagent for the gravimetric determination of potassium,<sup>2</sup> and the recent improvements in the technique of its

use,<sup>3</sup> it has become more readily feasible to devise a simple and accurate method for determining potassium even in a medium as complicated as sea water.

### METHOD

The procedure employed for the gravimetric determination of potassium was as previously described,<sup>3</sup> but with use of a 1 per cent. sodium tetraphenylboron solution instead of the more concentrated solution originally specified.

#### REAGENTS—

*Hydrochloric acid, concentrated.*

*Sodium tetraphenylboron solution*—Dissolve 5 g of solid sodium tetraphenylboron in 500 ml of water, add a few drops of phenolphthalein indicator and enough of *N* sodium hydroxide solution to turn the colour of the indicator pink. Filter if necessary. The solution so prepared is stable for at least 3 months.

*Saturated potassium tetraphenylboron wash solution*—Shake 1 litre of water with an excess of potassium tetraphenylboron precipitate (at room temperature). Filter immediately before use.

#### PROCEDURE—

Weigh accurately into a 250-ml conical flask 50 g of the sea water, add 3 ml of concentrated hydrochloric acid and place a rubber stopper in the flask; put it in an ice - water bath (0° C) for 15 minutes. Add to the cold solution 30 ml of the sodium tetraphenylboron reagent solution (previously also cooled to 0° C), mix the contents of the flask and place it in the ice - water bath for a few minutes.

Filter the mixture through a sintered-glass crucible, porosity No. 4, and wash the flask free of the precipitate with the saturated potassium tetraphenylboron wash solution (kept at room temperature), passing the washings through the crucible. Dry the crucible at 110° to 120° C for 30 minutes, cool in a desiccator and weigh.

Calculate the potassium content of the sample from the following formula—

$$\frac{\text{Weight of precipitate found} \times 0.1091 \times 100}{\text{Amount of sample taken}} = \text{potassium content, per cent.}$$

### RESULTS

In the first set of experiments artificial mixtures representing the concentrations of the more abundant ions in sea water were prepared. These solutions were then used for the preparation of mixtures with known amounts of added potassium. The results obtained on artificial sea water and on a solution containing twice the usual concentrations of the more abundant ions with and without added potassium and also solutions containing only pure potassium chloride are shown in Table I.

TABLE I  
DETERMINATION OF POTASSIUM IN ARTIFICIAL MIXTURES

Experiment number	Composition of sample	Potassium added, %	Potassium found, %	Difference, %	Remarks
1	50 ml of distilled water	0.0304	0.0304	-0.0000	—
2	50 ml of distilled water	0.0343	0.0342	-0.0001	—
3	50 ml of mixture 1*	nil	nil	—	No precipitate was formed after standing for 1 hour at 0° C
4	50 ml of mixture 1	0.0304	0.0308	0.0004	—
5	50 ml of mixture 1	0.0335	0.0337	0.0002	—
6	50 ml of mixture 2†	nil	nil	—	No precipitate was formed after standing for 1 hour at 0° C
7	50 ml of mixture 2	0.0304	0.0314	0.0010	—
8	50 ml of mixture 2	0.0338	0.0346	0.0008	—

\* Mixture 1 contains 0.040 per cent. of  $\text{Ca}^{++}$ , 0.127 per cent. of  $\text{Mg}^{++}$ , 0.0013 per cent. of  $\text{Sr}^{++}$  and 1.056 per cent. of  $\text{Na}^{+}$ , as chlorides, and 0.0026 per cent. of boric acid, and represents the concentrations of these ions in sea water.

† Mixture 2 contains twice the concentrations of ions in mixture 1.

These results show that the precipitation of potassium as the tetraphenylboron salt was quantitative under the conditions used and that the other metallic ions present in sea water caused a positive error of only about 1 per cent., which could hardly be considered significant. Even when the concentration of these ions was doubled, so giving an exaggerated degree of interference, the value for potassium was only about 3 per cent. higher than the theoretical. The larger concentration of these ions caused the formation of a finer precipitate, which was more difficult to wash free from the reaction mixture, and this might be the reason for the higher values found for potassium. There was no difficulty, however, in filtration in any of the three sets of experiments. No precipitate or turbidity was formed with the blank solutions even after standing for 1 hour at 0° C.

A set of determinations of potassium in sea water, obtained from the English Channel, was carried out. (The sample was taken from the beach at Eastbourne at high tide.) The procedure was exactly as described above, about 50 g of sample being used. The results obtained are shown in Table II.

TABLE II  
DETERMINATION OF POTASSIUM IN SEA WATER FROM THE ENGLISH CHANNEL

Experiment number	Weight of sample taken, g	Weight of potassium tetraphenyl-boron, g	Weight of potassium found, g	Potassium found, %
1	51.32	0.1850	0.02018	0.03932
2	50.47	0.1832	0.01999	0.03961
3	51.19	0.1856	0.02025	0.03955
4	50.86	0.1848	0.02016	0.03964
5	53.39	0.1930	0.02106	0.03945
6	50.98	0.1837	0.02004	0.03931
7	48.82	0.1773	0.01935	0.03964
8	51.47	0.1854	0.02023	0.03900
9	50.76	0.1851	0.02020	0.03979
10	51.15	0.1855	0.02024	0.03957
11	52.49	0.1902	0.02075	0.03953
12	48.89	0.1788	0.01951	0.03991

Mean = 0.03953

Standard deviation = 0.00024. Coefficient of variation = 0.61 per cent.

These results indicate a high degree of precision, which is consistent with the findings previously reported.<sup>3</sup> The calculated standard deviation of results<sup>4</sup> amounts to 0.00024 per cent. on the value of 0.03953 per cent. (average). This represents a deviation of well under 1 per cent., which is satisfactory.

The ratio of potassium to chlorine calculated from the average of these twelve values is 0.0207 (the chlorinity was determined by the Mohr method and found to be 19.095%<sub>oo</sub>). This is again in good agreement with the values reported by Barnes.<sup>1</sup>

TABLE III  
DETERMINATION OF POTASSIUM IN "Eau de mer normale,"  
11/7/54, CHLORINITY 19.373%<sub>oo</sub>

Experiment number	Weight of sample taken, g	Weight of potassium tetraphenyl-boron, g	Weight of potassium found, g	Potassium found, %
1	49.33	0.1842	0.02010	0.04075
2	50.22	0.1850	0.02018	0.04019
3	50.60	0.1879	0.02050	0.04051
4	24.84	0.0911	0.00994	0.04000
5	24.62	0.0908	0.00991	0.04025
6	24.65	0.0910	0.00993	0.04029

Mean = 0.04033

Standard deviation = 0.000263. Coefficient of variation = 0.60 per cent.

The final testing of the method was performed by determining the potassium content of a sample of "Eau de mer normale," the international standard of sea water. The results obtained on 50-g and 25-g samples are shown in Table III. (When 25 g of sample were used the amounts of hydrochloric acid and sodium tetraphenylboron reagent were halved.)

The precision of the results shown in Table III is good and compares well with the values from Table II. The ratio of potassium to chlorine calculated from the average of the six values was 0.0208, which again agrees closely with the value given in Table II.

#### DISCUSSION OF RESULTS

The method based on the precipitation of potassium as the tetraphenylboron salt is, in view of the results shown above, capable of giving reproducible and accurate results, at the same time being the simplest and most rapid of all the methods that can be used for the same purpose. When applied to testing sea water, it requires no preliminary separation of potassium from the sample, and owing to the very high insolubility and ease of handling the precipitate the determination can be performed on a macro or a micro scale.

For higher accuracy the values found could be corrected for the positive bias indicated by experiments 4 and 5 in Table I (0.0003 per cent. mean), but as this value was smaller than that found for the standard deviation of results no attempt was made in this work to change the experimental figures.

I thank Plant Protection Ltd. for permission to carry out this work, which was outside the usual scope of their business, and Dr. H. Barnes, Marine Station, Isle of Cumbrae, Scotland, for his gift of a sample of the international standard of sea water and for his helpful criticism. The reagent required in this work was kindly supplied by L. Light & Co. Ltd., Colnbrook, England.

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TECHNICAL DEPARTMENT  
PLANT PROTECTION LIMITED  
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## A Simplified Form of Coulometric Titration

By J. S. HETMAN\*

A method of simplified coulometric titration with use of an internal current source is described. By this means it is possible to control the current accurately. Details are given of the use of this method in the determination of chromium and vanadium in alloy steels, a potentiometer with a Magic Eye indicator being used to determine the end-point.

In coulometric titrations a chemical substance is neutralised, oxidised or reduced at the electrodes by the electric current. The quantities are then determined from Faraday's laws. Titrating solutions and burettes are not required.

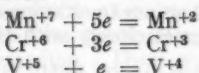
In this simplified method, which is an extension of the work of Oelsen, Haase and Graue,<sup>1</sup> the current is produced within the apparatus by using a zinc electrode system immersed in the solution under test, but separated from it by a permeable membrane, and connected through an ammeter and a platinum electrode also immersed in the solution. The current can be easily regulated by variation of the depth of immersion of the zinc electrode.

The progress and end-point of the titration can be followed and determined by means of the potentiometer. A clear and definite end-point indication is given by the use of a Mullard Magic Eye potentiometer.

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Such coulometric titrations can be applied to the determination of chromium and vanadium in steels. The apparatus required is comparatively simple and determinations can be carried out rapidly. The method is applicable to carrying out a series of works tests.

The method lends itself particularly to reduction reactions, since the short-circuited platinum electrode acts as a cathode—



In the presence of excess of ferric iron, ferrous ions are produced on the cathode in accordance with the following equation—



these ions react with reducible permanganate, dichromate or vanadate.

From Faraday's laws—

for  $\text{Mn}^{+7} \rightarrow \text{Mn}^{+2}$ , 1.0 coulomb = 0.114 mg of manganese,  
 for  $\text{Cr}^{+6} \rightarrow \text{Cr}^{+3}$ , 1.0 coulomb = 0.180 mg of chromium, and  
 for  $\text{V}^{+5} \rightarrow \text{V}^{+4}$ , 1.0 coulomb = 0.528 mg of vanadium.

Potentiometric control of such redox<sup>2</sup> reactions is particularly applicable, since by the use of small currents the value of  $\Delta V$  ( $V$  = volume of reagent) in the ratio  $\frac{\Delta E}{\Delta V}$  is very small, giving complete agreement in the relation—

$$\frac{\Delta E}{\Delta V} = \text{maximum at equivalence point, or } \frac{dE}{dC} = \pm \frac{0.058}{nC},$$

where  $C$  = concentration of titrant,

and  $\frac{dE}{dC}$  is obtained from  $E = E_0 \pm \frac{RT}{nF} \log C$ .

#### EXPERIMENTAL EXAMPLES

##### APPARATUS—

The lay-out of the apparatus is shown in Fig. 1.

*Potentiometer*, Mullard Type E92/2. In order that the Magic Eye can be watched, and at the same time a check kept on the current, it is advisable to fit an extension lead about a metre long from the potentiometer to the Magic Eye tube. Thus the Magic Eye can be set in a position close to the ammeter. The Cambridge portable pH meter could be used very successfully by application of Muller's method of titration.<sup>3</sup>

*Zinc rod*, 15 cm long, 7 mm in diameter, fitted to suitable racking. The rod should be prepared from analytical-reagent grade zinc.

*Glass tube*, 15 cm long, 20 mm in internal diameter, covered on lower end with permeable collodion membrane and filled with dilute sulphuric acid solution (1 + 20).

*The membrane* is prepared by dissolving pyroxylin in a mixture of ethanol and ether (1 + 2). Sufficient of this solution is spread on the convex surface of a watch-glass and left for about 5 minutes. The semi-solid membrane is placed over the open end of the glass tube and secured by spreading a little of the original solution around the edges. A good membrane should hold distilled water.

*Platinum cathode*, a gauze electrode 11 cm by 5 cm.

*Indicator and reference electrodes*, platinum wire as indicator electrode; saturated calomel half cell or silver iodide as reference electrode.

The silver iodide electrode is prepared by dipping the end of a platinum wire (1 mm in diameter) in molten silver iodide to a depth of 15 mm. The remainder of the wire is isolated by covering with a solution of vinyl acetate in a mixture of toluene and ethanol (4 + 1).

*Precision milliammeter*.

*Stop-watch*.

*Magnetic stirrer*.

*A 400-ml beaker*.

In the work reported in this paper platinum has been used as an indicator electrode and saturated calomel or silver iodide as a reference electrode.

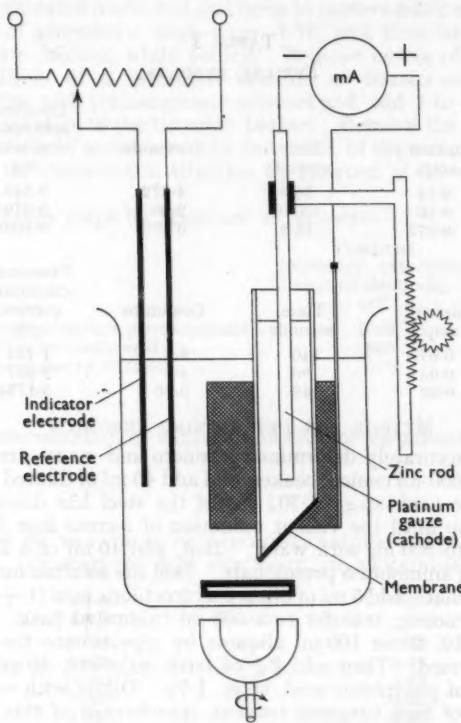


Fig. 1. Apparatus for coulometric titration

#### METHOD OF TITRATION—

For this purpose consider the titration of standard potassium permanganate.

Take 40 ml of diluted sulphuric acid (1 + 3) in the 400-ml beaker and dilute to 200 ml with water. Add 1 g of ferric sulphate and then a known volume of 0.1 N potassium permanganate solution. Fill the glass tube with dilute sulphuric acid (1 + 20). Introduce the tube and electrodes into the beaker. Switch on the stirrer. Connect the platinum gauze to the positive terminal on the ammeter and the zinc rod to the negative terminal. Connect the indicator electrode and the reference electrode to the potentiometer. On the maximum sensitivity setting of the potentiometer bring the Magic Eye to the fully open position. Immerse the zinc rod in the tube and immediately start the stop-watch, noting the ammeter reading.

The approach of the end-point is indicated by a flickering of the Magic Eye. The final end-point, which is very definite, is noted by the instantaneous closing of the Magic Eye. Stop the watch.

Titration of 0.1 N potassium dichromate is carried out in exactly the same way, except that 10 ml of phosphoric acid, sp.gr. 1.70, are introduced into the beaker to increase the sensitivity of the Magic Eye. Typical results for both titrations are shown in Table I.

The accuracy of timing is of course subject to human error and thus dependent upon the experience of the operator. For the highest accuracy it is essential to obtain the following conditions: (a) a sufficient excess of ferric ions, (b) vigorous stirring of the solution, and (c) the performance of the titration on the same current.

## STABILITY OF THE CURRENT—

Usually the current remains constant throughout the titration, but in case of any variation, stabilising could be done by rapid adjustment of the depth of immersion of the zinc rod.

TABLE I  
TYPICAL RESULTS

Volume of 0.1 N potassium permanganate, ml	Current, amp.	Time, seconds	Coulombs	Theoretical manganese content, mg	Manganese found by titration, mg
0.5	0.14	34.8	4.872	0.549	0.555
0.2	0.10	20.0	2.00	0.2197	0.228
0.1	0.072	13.6	0.979	0.1098	0.1116

Volume of 0.1 N potassium dichromate, ml	Current, amp.	Time, seconds	Coulombs	Theoretical chromium content, mg	Chromium found by titration, mg
1.0	0.07	140	9.8	1.734	1.764
0.5	0.05	96	4.8	0.867	0.864
0.1	0.02	48	0.96	0.1734	0.1728

## METHOD FOR DETERMINING CHROMIUM

Chromium can be accurately determined in micro and macro amounts.

Put 1 g of steel in a 600-ml conical beaker, and add 40 ml of diluted sulphuric acid (1 + 3) and 10 ml of phosphoric acid, sp.gr. 1.70. After the steel has dissolved, add nitric acid, sp.gr. 1.42, drop by drop until the violent oxidation of ferrous iron is over, boil and fume for 5 minutes. Dilute to 200 ml with water. Boil, add 10 ml of a 5 per cent. solution of silver sulphate and 5 g of ammonium persulphate. Boil the solution for 10 minutes to decompose the excess of persulphate, add 5 ml of diluted hydrochloric acid (1 + 3) and boil vigorously for 10 minutes. After cooling, transfer to a 500-ml calibrated flask. Depending upon the chromium content put 10, 20 or 100-ml aliquots by pipette into the beaker in which the titration is to be performed. Then add 2 g of ferric sulphate, 40 ml of diluted sulphuric acid (1 + 3) and 10 ml of phosphoric acid, sp.gr. 1.70. Dilute with water until the volume is 200 ml. With steels of high tungsten content, interference of this element is prevented by the further addition of phosphoric acid.

The excess of phosphoric acid will also remove free ferric ions and make the titration impossible. It has been found that 1 g of iron combines with 15 ml of phosphoric acid, therefore it is simple to know if excess of iron is present. If the steel contains vanadium, it will be titrated as chromium.

## NOTE—

If vanadium is present and its determination is required, the boiling with 5 ml of hydrochloric acid should be omitted and the permanganate should be removed by the dropwise addition of 0.25 N oxalic acid to the warm solution.<sup>4</sup> By this procedure the loss of vanadium as the volatile compound  $\text{VOCl}_3$  is avoided.

## RESULTS—

Results for the determination of chromium in Armco iron B.C.S. No. 150 are shown in Table II.

TABLE II

## DETERMINATION OF CHROMIUM IN ARMCO IRON, B.C.S. NO. 150\*

Weight of steel, g	Current, amp.	Time, seconds	Coulombs	Chromium found, %
1.000	0.022	33	0.725	0.013
1.000	0.03	24	0.720	0.0130
1.000	0.02	35	0.700	0.0126

\* Average analysis: C, 0.035 per cent.; Si, 0.030 per cent.; S, 0.020 per cent.; P, 0.008 per cent.; Mn, 0.044 per cent.; As, 0.03 per cent.; Cr, 0.01 per cent.; Cu, 0.07 per cent.

## METHOD FOR DETERMINING VANADIUM

Vanadium can be determined in semi-micro and macro amounts.

Dissolve the sample in 30 to 40 ml of diluted sulphuric acid (1 + 3). Oxidise with a few millilitres of concentrated nitric acid and fume to remove nitric acid completely. Dilute to 100 ml, add 10 ml of phosphoric acid, sp.gr. 1.70, and then oxidise by adding 0.25 N potassium permanganate solution while boiling. Remove excess of permanganate solution by the dropwise addition of a saturated solution of ferrous sulphate. Cool to room temperature. Re-oxidise with permanganate solution and add 1 to 2 ml in excess. Add 1 g of ferric sulphate, and transfer to the titration beaker. Remove the excess of permanganate by means of 0.25 N oxalic acid and observe the end-point of the reduction potentiometrically, after which carry out the coulometric titration by insertion of the zinc electrode as already described.

Typical readings taken stage by stage are as follows—

	Potential (platinum - saturated- calomel electrode), mV	Potential (platinum - silver iodide electrode), mV
Stage 1: excess of potassium permanganate..	1060	800
Stage 2: reduction by oxalic acid ..	850	400
Stage 3: after coulometric titration ..	520	240

## RESULTS

Results for the determination of vanadium in chrome-vanadium steel B.C.S. No. 224 are shown in Table III.

TABLE III

DETERMINATION OF VANADIUM IN CHROME-VANADIUM STEEL B.C.S. NO. 224\*  
CONTAINING 0.24 PER CENT. OF VANADIUM

Weight of steel, g	Current, amp.	Time, seconds	Coulombs	Vanadium found, %
0.7230	0.050	69	3.45	0.252
0.9984	0.080	56	4.48	0.237
0.3390	0.040	38	1.52	0.232
0.2584	0.050	24	1.20	0.246
0.2584	0.030	40	1.20	0.246

\* Average analysis: Cr, 1.46 per cent.; V, 0.24 per cent.; C, 0.390 per cent.; Si, 0.30 per cent.; P, 0.012 per cent.; Mn, 0.695 per cent.; Ni, 0.10 per cent.; Cu, 0.07 per cent.; Mo, 0.02 per cent.

## APPLICATIONS OF THE METHOD

Sometimes, when classical methods are difficult to apply, the coulometric titration method is very useful. Results are given in Tables IV and V of chromium and vanadium determinations on a low-alloy steel and on a high-speed steel. For each steel the chromium and vanadium have first been determined together, and then the vanadium by a separate titration, the chromium content being calculated by difference. Different weights of sample can be used and then allowance can be made in the calculation.

TABLE IV

## DETERMINATION OF CHROMIUM AND VANADIUM IN LOW-ALLOY STEEL B.C.S. NO. 251\*

Weight of steel, mg	Chromium plus vanadium			Vanadium			Vanadium found, %	Chromium found, %
	Current, amp.	Time, seconds	Coulombs	Weight of steel, mg	Current, amp.	Time, seconds		
500	0.070	22	1.54	500	0.048	8	0.32	0.034
500	0.065	24	1.58	500	0.020	17	0.34	0.036
500	0.050	32	1.60	500	0.020	16	0.32	0.034
500	0.050	31	1.55	500	0.030	11	0.33	0.035
500	0.050	32	1.60	500	0.030	12	0.36	0.038

\* Average analysis: Cr, 0.044 per cent.; V, 0.0334 per cent.; Mo, 0.185 per cent.; Ni, 5.15 per cent.; Mn, 0.165 per cent.; Si, 0.013 per cent.; Cu, 0.090 per cent.

TABLE V

## DETERMINATION OF CHROMIUM AND VANADIUM IN HIGH-SPEED STEEL B.C.S. No. 220\*

Weight of steel, mg	Chromium plus vanadium			Weight of steel, mg	Vanadium			Vanadium found, %	Chromium found, %
	Current, amp.	Time, seconds	Coulombs		Current, amp.	Time, seconds	Coulombs		
25	0.065	110	7.15	250	0.060	110	6.6	1.3	4.67
25	0.060	120	7.20	250	0.080	81	6.48	1.37	4.72
25	0.090	80	7.20	250	0.100	65	6.50	1.37	4.72
50	0.095	148	14.04	500	0.090	145	13.05	1.38	4.58
50	0.100	138	13.8	500	0.100	130	13.00	1.37	4.50
50	0.100	140	14.0	500	0.100	130	13.00	1.37	4.57

\* Average analysis: W, 6.74 per cent.; Mo, 4.17 per cent.; Cr, 4.61 per cent.; V, 1.35 per cent.; Co, 0.67 per cent.; C, 0.88 per cent.; Si, 0.30 per cent.; Mn, 0.25 per cent.

Vanadium can be repeatedly titrated on the same sample by re-oxidation and repeating the procedure; with high tungsten-molybdenum steels the first titration always gives high results, but no difficulty is experienced after re-oxidation and further titration.

I express to the Directors of Ruston and Hornsby Ltd. my sincere thanks for permission to publish.

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RUSTON & HORNSBY LTD.  
LINCOLN

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Amended, February 20th, 1956

## A Micro-scale Spot-test for Nicotine

By P. LUIS

The test is particularly suitable for the detection of nicotine in forensic work, and has been successfully applied to mixtures containing tobacco and to urine samples.

Two new tests for nicotine based on the oxidation of the alkaloid in a buffered acid medium have been published. In the first, the oxidation was performed with potassium persulphate and, on addition of sodium thiosulphate, sodium nitroprusside and ammonium hydroxide, an intense wine-red colour developed.<sup>1</sup> In the second, the oxidation was carried out with lead peroxide or sodium bismuthate; the excess of oxidant was destroyed and, after addition of concentrated sulphuric acid, a strong red coloration was obtained.<sup>2</sup>

While the oxidation products were being studied, it was observed that certain extracts showed a green-blue coloration, and this fact suggested the possibility of a new colour reaction for nicotine. The alkaloid was oxidised as described above, and the resulting solution was partly neutralised with sodium bicarbonate or calcium carbonate; the residue on evaporation was green-blue in colour. The test has been improved and simplified by making use of a micro procedure in which neutralisation is not necessary. When properly performed, the test is specific, reliable and sensitive, and it is little affected by interferences. For these reasons it is particularly suitable for the detection of nicotine in the extracts produced by the Stas - Otto method, in urine, tobacco and tobacco smoke and so on.

Mameli<sup>3</sup> states that concentrated sulphuric acid and nicotine give a colourless to yellow solution, but that concentrated sulphuric acid and hydrogen peroxide (Shaer's reagent) give a negative reaction. According to Bauer,<sup>4</sup> nicotine gives a red-brown coloration on addition of Shaer's reagent, but I have not found this to be so, and the test seems to be

valueless for nicotine. Schindelmeister's test for nicotine is based on oxidation with nitric acid in the presence of formaldehyde or formic acid, when a pink colour develops; it is not related to the proposed test, as the oxidation products of nicotine with nitric acid are different from those with other oxidising agents.

### METHOD

#### REAGENTS—

*Sodium bismuthate*—Analytical-reagent grade.

*Phosphate - acetic acid solution*—Dissolve 15.5 g of monosodium orthophosphate and 4 g of disodium orthophosphate in about 35 ml of hot water, cool the solution somewhat, add 50 ml of glacial acetic acid and make up to 100 ml with water. This solution keeps well.

*Oxidising suspension*—Triturate carefully 0.10 g of sodium bismuthate with 0.3 to 0.4 ml of the phosphate - acetic acid solution in a small mortar, and make up to 5 ml with the same solution. This reagent deteriorates rapidly and must be renewed after 2 hours.

#### PROCEDURE—

Into a capillary pipette of about 1 mm diameter put about 1.5 to 2 mm of the oxidising suspension, keeping it well stirred, dry the end with cotton-wool or filter-paper and then add about twice the volume of the nicotine test solution (Fig. 1a). With slight tapping make the mixture run 1 to 2 cm into the capillary and then seal the end by means of a micro burner (Fig. 1b). Make the solution run to the bottom of the capillary by means of slight tapping (Fig. 1c) and then immerse the capillary in boiling water for 2 minutes. Then place it in a centrifuge, spin it and cut away the precipitate (Fig. 1d). Transfer the remaining clear solution to a porcelain dish or crucible, and put the dish on a steam-bath. As the evaporation progresses, the residue gradually takes on a blue or blue-green coloration, especially near the edge of the droplet.

It is advisable to perform the test in rather dilute solution, say 1:5000 to 1:20,000, as otherwise the colour will be too dark. The test will detect 0.075 µg of nicotine in 3 cubic millimetres of solution, the limiting concentration being 1 part in 40,000.

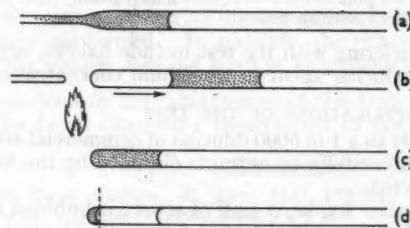


Fig. 1 (a) to (d). Sequence of operations with capillary tubes

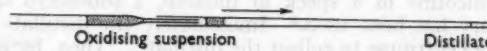


Fig. 2. Technique for introducing oxidising suspension into capillary tube

The reaction can also be carried out in a micro centrifuge tube: two drops of the nicotine solution and a drop of the oxidising suspension are put in the tube and it is immersed for 2 minutes in boiling water, then centrifuged, and the clear solution is withdrawn and evaporated in a porcelain dish as described above.

#### SPECIFICITY OF THE TEST

The reaction was performed on numerous natural and synthetic basic compounds, pyridine and so on. From the results summarised below it can be seen that the test is little affected by interferences.

Alkaloids that do not interfere with the test even when present at concentrations twenty times greater than that of the nicotine include—

*Purine group*: caffeine, theobromine, theophylline;

*Tropine group:* atropine, hyoscyamine, homatropine, hyoscine, atropine methobromide, cocaine, ecgonine;

*Cinchona group:* quinine, quinidine, cinchonine, cinchonidine;

*Other alkaloids:* aconitine, aspidospermine, coniine, duboisine, ephedrine, emetine, sparteine, strychnine, lobeline, pelletierine, pilocarpine, solanine, veratrine, yohimbine.

Other substances that do not interfere with the test even when present at concentrations forty times greater than that of the nicotine include—

*Pyridine group:* pyridine, nicotinic acid, nicotinamide, nikethamide, isoniazid;

*Various:* ammonia, Benadryl, stovaine, phenobarbitone, proteins.

The reactions of some alkaloids and related compounds that interfere partly or totally with the test for nicotine are shown in Table I.

TABLE I  
REACTIONS OF INTERFERING ALKALOIDS

Substance	Colour of resulting solution	Colour of residue	Reaction of a mixture of 0.5 to 1 $\mu$ g of nicotine and 3 to 5 $\mu$ g of substance
Colchicine	yellow	brownish	weak
Physostigmine	pink	reddish brown	weak
Morphine	yellowish	brownish	doubtful to weak
Ethyl morphine	yellowish	brownish	doubtful to weak
Codeine	yellowish	brownish	doubtful to weak
Diacetylmorphine	yellowish	brownish	doubtful to weak
Narcotine	yellowish	brownish	doubtful to weak
<i>apo</i> Morphine	blue	blue-black	interference
Narceine	yellow	reddish brown	interference
Papaverine	yellow	brown	interference
Brucine	brownish yellow	reddish brown	interference
Adrenaline	pink	dark brown	interference
Procaine	brownish yellow	brown	interference

Certain other compounds interfering with the test include halides, organic acids, sugars in high concentrations and any reducing agent in a medium concentration.

#### APPLICATIONS OF THE TEST

The test can be applied directly to a 1 in 5000 dilution of commercial 40 per cent. nicotine sulphate. It may also be used successfully on extracts obtained by the Stas - Otto method when nicotine poisoning is suspected.

For detecting nicotine in tobacco smoke, a puff of smoke is bubbled through a mixture of 0.3 ml of water and 1 drop of phosphate - acetic acid solution. The test is then performed with 4 to 5 cubic millimetres of the resulting solution. Distinct positive reactions have been observed.

For detecting nicotine in a speck of tobacco, a sub-micro steam-distillation of the tobacco in a capillary has been used.<sup>5</sup> Immediately the distillate has been obtained, the capillary is spun in a centrifuge to collect the distillate. Then, by means of a fine capillary, about one-third to one-half of the oxidising reagent is introduced into the capillary tube (Fig. 2), which is then spun gently in a centrifuge. The bottom of the capillary tube is then tapped to produce a suspension, which is used for the test.

When nicotine is being tested for in mixtures containing interfering substances, such as those given in Table I, which give strongly coloured compounds on oxidation, or in the presence of reducing substances, it is advisable to separate the nicotine by a sub-micro steam-distillation. This procedure has been successfully applied in a forensic case to a black-coffee residue that had been mixed with cigarette tobacco. It was also successful for mixtures of nicotine and procaine hydrochloride, organic acids, halides and so on. The limiting concentration of nicotine was 1 in 10,000, and that of other substances was 1 in 20.

#### DETECTION OF NICOTINE IN URINE—

To a 7 to 8-ml sample of urine in a centrifuge tube are added one drop of concentrated hydrochloric acid and 5 ml of light petroleum. A rubber stopper is placed in the tube, which

is then shaken vigorously for 2 minutes. In order to destroy the foam a few drops of ethanol are added. The tube is spun gently in a centrifuge and, if the foam still persists, a few more drops of ethanol are added. The clear upper layer is withdrawn by means of a dropping tube and is rejected. The remaining solution is made strongly alkaline by adding a few drops of concentrated sodium hydroxide solution. The urine is then extracted with 4 ml of light petroleum, as described above, the foam being again destroyed by means of ethanol. The tube is spun gently in the centrifuge and, if the separation is not satisfactory, a few additional drops of ethanol will be required. The clear upper liquid is transferred to a small porcelain dish. A drop of glacial acetic acid and then a drop of water are added, and the solvent is removed by evaporation on a water-bath. The residue (having a volume of about 80 cubic millimetres) contains the nicotine, and about 5 cubic millimetres are used for the test. When the test is negative, it is advisable to concentrate the residue to about 20 cubic millimetres and to repeat the test.

Good results were obtained for the urine of non-smokers to each sample of which 1  $\mu$ g of nicotine had been added. Fairly good results were obtained for the urine of moderate smokers.

#### DISCUSSION

The proposed reaction is simpler than the others that I have published,<sup>1,2</sup> and gives good results over a wide range of concentrations. Of the three tests for nicotine, the first,<sup>1</sup> in spite of being very sensitive, is affected by interferences. The second,<sup>2,5</sup> apart from being specific and very sensitive, is scarcely affected by interferences, and so it was considered "as the best and most reliable test for nicotine." As the test described in this paper shows a high degree of sensitivity and specificity, it is advisable to perform both tests simultaneously, as they are equally reliable and appear to be better than any known colour reaction for nicotine.

Of all the oxidising agents tried, sodium bismuthate seems to be the best. It has the high potential required and its insolubility permits its separation by centrifugation after the oxidation has been accomplished.<sup>2</sup> It was also established that the controlled oxidation of nicotine requires a high potential acidity, provided by the excess of acetic acid and the acid phosphate, which also increases the rate of the reaction, because the phosphate ions remove the bismuth ions as they are formed. In addition, the mixture has a great buffering capacity, and so the pH of the sample does not have to be adjusted.

This work was done in the laboratories of the University of Buenos Aires, School of Pharmacy, and the Legal Chemistry Department of the Federal Police.

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ROSARIO 2021

CASTELAR, BUENOS AIRES  
ARGENTINE

November 28th, 1956

#### Notes

##### THE DETERMINATION OF CALCIUM IN RAIN-WATER

THE standard method<sup>1</sup> for determining calcium in rain-water from atmospheric-deposit gauges is time-consuming. Although the use of ethylenediaminetetra-acetic acid (EDTA) avoids the double precipitation of oxalate, masking of the cupric ion introduced as an algicide is needed, and the evaporation of large quantities of water to small bulk is still frequently necessary.

The use of the flame photometer overcomes the need for evaporation, but preliminary experiments with an EEL instrument (Evans Electroelenium Ltd.) calibrated with pure calcium chloride solutions gave poor agreement with the standard method. When the instrument was calibrated with a solution simulating London rain-water, the agreement was much improved.

To compare the methods, thirty-three samples of rain collected in the London area were examined by each method, with the results shown in Table I. The details of the non-standard methods are given below.

TABLE I

## COMPARISON OF RESULTS

Gauge number	Calcium found by		
	Standard method, tons per sq. mile	EDTA method, tons per sq. mile	Flame-photometer method, tons per sq. mile
1	0.66	0.64	0.66
2	0.61	0.61	0.59
3	0.62	0.69	0.61
4	0.99	1.00	1.10
5	0.80	0.87	0.77
6	0.63	0.63	0.66
7	1.02	1.00	1.08
8	0.62	0.60	0.67
9	0.52	0.52	0.59
10	0.77	0.83	0.87
11	1.70	1.66	1.79
12	2.05	2.05	2.18
13	1.40	1.32	1.48
14	0.92	0.87	0.95
15	0.77	0.84	0.87
16	0.91	0.90	0.99
17	0.86	0.83	0.97
18	0.60	0.61	0.67
19	1.35	1.31	1.35
20	0.58	0.57	0.62
21	1.02	1.04	1.02
22	1.02	1.04	1.07
23	0.49	0.48	0.53
24	2.16	2.20	2.27
25	1.63	1.52	1.70
26	1.65	1.52	1.67
27	2.65	2.41	2.62
28	1.85	1.62	1.73
29	1.09	1.02	0.94
30	1.56	1.43	1.58
31	1.60	1.43	1.63
32	1.47	1.33	1.40
33	1.73	1.76	1.61

## EXPERIMENTAL

## EDTA METHOD—

A convenient quantity of rain-water is evaporated to about 100 ml, and 2 ml of 4 N sodium hydroxide solution, 1 ml of 0.3 per cent. potassium cyanide solution and about 0.2 g of murexide indicator are added. It is then titrated with 0.02 N EDTA solution.

## FLAME-PHOTOMETRIC METHOD—

The instrument is used in accordance with the maker's instructions. For calibration, a solution of the following composition is prepared with reagent grade chemicals—

Calcium carbonate	..	..	0.5 g
Ammonium chloride	..	..	0.08 g
Sodium chloride	..	..	0.13 g
Cupric sulphate, crystals	..	..	0.02 g
Sulphuric acid, concentrated	..	..	1 ml

These are dissolved in water and made up to 100 ml; 1 ml of this solution diluted to 100 ml with distilled water gives a solution containing 20 p.p.m. of calcium.

## DISCUSSION OF RESULTS

The regression equations for predicting the result of the standard method from the result of the alternatives are—

(a) EDTA result  $\times 1.096 - 0.06$  = standard result in tons per sq. mile.

(b) Flame-photometric result  $\times 1.018 - 0.05$  = standard result in tons per sq. mile.

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For both equations the standard deviation not due to linear regression amounts to 0.07 tons per sq. mile, or about 6 per cent. of the result.

The precision of the standard deposit gauge is dependent upon the material being examined. Two gauges side by side gave standard deviations of 13 per cent. and 27 per cent. of the mean for chloride and sulphate ions, respectively.<sup>2</sup> It thus appears probable that for the level of calcium found in London deposit gauges (0.3 to 3.0 tons per sq. mile) either alternative method gives results to an accuracy within the sampling error of the gauge, although the flame-photometer is closer to the standard.

We thank Mr. H. V. Pugh, Controller of London Division, Central Electricity Authority, for permission to publish this Note, Mr. E. A. Howes, Divisional Chief Chemist, for suggesting the problem, and Mr. D. D. Collins and Mr. I. Riseman for assistance.

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CENTRAL ELECTRICITY AUTHORITY, LONDON DIVISION  
GENERATION OPERATIONS DEPARTMENT (CHEMISTRY SECTION)  
BATTERSEA GENERATING STATION  
KIRTLING STREET  
LONDON, S.W.8

I. DAVIES  
G. HOPKINSON  
January 30th, 1956

### THE SEPARATION AND DETERMINATION OF TRACES OF LEAD IN THE PRESENCE OF SMALL AMOUNTS OF BISMUTH

DURING the determination of small amounts of lead, the lead is generally precipitated as the chromate in weak acetic acid solution; the precipitate is filtered off, washed and dissolved in dilute nitric acid and the solution is treated with diphenylcarbazide to produce a "permanganate" colour, which is compared against standards.<sup>1</sup>

If bismuth is present, under the same conditions some or all of it is precipitated as the dichromate, which also yields the same colour with diphenylcarbazide, thus interfering with the lead determination.

Many known methods were tried in an attempt to separate the lead and bismuth and so eliminate this interfering effect.

#### EXPERIMENTAL

##### CITRIC ACID SEPARATION—

A 0.5-g portion of citric acid was added to the mixture of lead chromate and bismuth dichromate just before filtration.<sup>2</sup> All the bismuth dichromate dissolved, but some of the lead chromate did also. For 0.100 mg of lead present only 0.081 mg was recovered. This method is only applicable for the separation of bismuth from large amounts of lead. A modification of this method was then carried out. During the precipitation of the chromate and the dichromate the solution is finally acidified with diluted acetic acid (1 + 1 v/v) and two drops are added in excess. Citric acid was used instead of acetic acid, but once again the recovery was approximately 80 per cent.

##### ELECTROLYTIC SEPARATION—

A small amount of copper nitrate was added to a nitric acid - sulphuric acid solution of the lead and bismuth, and deposition in accordance with the normal electrolytic determination of copper was carried out. Although all the bismuth was recovered from the cathode,<sup>3</sup> and no lead dioxide was deposited on the anode, only 90 per cent. of the lead remained in the solution.

##### DOUBLE DITHIZONE EXTRACTION—

After dithizone extraction of lead and bismuth at pH 11, the chloroform layer was shaken with 1 per cent. v/v nitric acid to extract the lead, the bismuth remaining in the chloroform layer.<sup>4</sup> Recovery of lead was between 90 and 120 per cent., indicating incomplete extraction of lead on occasions and slight extraction of bismuth on others.

A different attack was then made.

## SEPARATION OF SULPHIDES WITH 2 N HYDROCHLORIC ACID—

After dithizone extraction at pH 11, the chloroform layer, containing lead and bismuth, was evaporated to dryness, organic matter was destroyed and the residue was dissolved in 25 ml of 2 N hydrochloric acid containing 0.02 g of copper. The solution was treated with hydrogen sulphide gas, brought to the boil, again treated with hydrogen sulphide, and, after addition of paper pulp, filtered, the precipitated sulphides being washed with 2 N hydrochloric acid saturated with hydrogen sulphide.

Recovery of lead in the filtrate was excellent, the bismuth being completely separated as the sulphide with the copper sulphide.

## RESULTS

The results in Tables I and II show the clean separation of the lead from the bismuth under these conditions, and the results in Table III show the errors likely to occur if no separation is carried out.

TABLE I

## RECOVERY OF LEAD IN PRESENCE OF 0.5 MG OF BISMUTH

Lead added, mg	..	..	0.000	0.100	0.140	0.180	0.220	0.260
Lead found, mg	..	..	0.004	0.104	0.146	0.183	0.220	0.260
Lead recovered, mg	..	..	—	0.100	0.142	0.179	0.216	0.256
Bismuth recovered from sulphides, mg			0.503	0.502	0.498	0.500	0.503	0.500
Bismuth in filtrate, mg	..	..	nil	nil	nil	nil	nil	nil

TABLE II

## RECOVERY OF LEAD IN PRESENCE OF 2 MG OF BISMUTH

Lead added, mg	..	..	0.000	0.100	0.200
Lead found, mg	..	..	0.013	0.113	0.220
Lead recovered, mg	..	..	—	0.100	0.207
Bismuth recovered from sulphides, mg			2.00	2.00	2.00
Bismuth in filtrate, mg	..	..	nil	nil	nil

TABLE III

## ERRORS INTRODUCED BY DETERMINING LEAD WITHOUT SEPARATING BISMUTH

Bismuth present, %	..	..	0.177	0.0177	0.0144
Lead present, %	..	..	0.004	0.0077	0.0024
Lead found (no separation of bismuth), %	..	..	0.072	0.0136	0.0127

## CONCLUSIONS

Bismuth can be separated from lead by co-precipitating with copper sulphide in 2 N hydrochloric acid, the lead passing into the filtrate. This separation is necessary if the chromate precipitation is to be carried out, as the bismuth is also precipitated with the lead at this stage, and causes high results.

I acknowledge my indebtedness to the Roan Antelope Copper Mines Limited, for permission to publish this method.

## REFERENCES

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## CHEMICAL LABORATORY

ROAN ANTELOPE COPPER MINES LIMITED  
LUANSHYA, NORTHERN RHODESIA

V. J. MOORE

First submitted, July 11th, 1955  
Amended, March 26th, 1956

### THE DETERMINATION OF SMALL AMOUNTS OF BISMUTH IN COPPER MATTES AND CONCENTRATION PRODUCTS

THE determination of traces of bismuth becomes straightforward if the bismuth can be isolated with copper, added during the determination or initially present in the sample.

Bismuth has been determined electrolytically by using graded potentials, but equipment is expensive and not easily adapted for large numbers of routine determinations.<sup>1</sup> Scott and Furman found that samples containing less than 0.03 g of bismuth could be deposited satisfactorily in the presence of sulphuric acid.<sup>2</sup> It has been observed that bismuth is deposited on both anode and cathode<sup>3</sup> and that bismuth is only partly deposited during the normal electrolytic deposition of copper.<sup>4</sup> Neither of these last two observations applies when the bismuth is present in small amounts.

It has been found that small amounts of bismuth are deposited completely with, and at the same time as, copper during electrolysis under the same conditions used when copper is being determined electrolytically. This fact was also noted by Young.<sup>5</sup>

The usual method for determining small amounts of bismuth involves, at one stage, the separation of the copper and bismuth from the iron as sulphides and the performance of a wet combustion on the paper and sulphides, the manipulation of both being rather awkward.<sup>6</sup> If any carbon remains undestroyed at this stage, the bismuth content, if determined colorimetrically, will appear to be high. By using the electrolytic method these steps are avoided, the method is shortened considerably and manipulation is made easier.

#### METHOD

Weigh out 1 g of sample into a 300-ml Erlenmeyer flask. If sulphides are present, add 2 ml of bromine - acetic acid mixture (1 + 1 v/v), and set aside for 5 minutes; then add 10 ml of concentrated nitric acid, set aside for a further 5 minutes, and add 5 ml of concentrated sulphuric acid. Heat to fumes and fume for 5 minutes. If sulphides are absent, add 10 ml of concentrated nitric acid and 5 ml of concentrated sulphuric acid, and heat to fumes and fume for 5 minutes.

Cool, add 30 ml of 10 per cent. v/v nitric acid, boil, filter off and wash insoluble matter, and electrolyse the filtrate at 2 amps. until deposition has finished. Wash down the cover glasses and add the equivalent of 0.05 g of copper as a copper nitrate solution and pass the current for a further 5 minutes. This gives the copper - bismuth deposit a protective sheath of copper and eliminates loss due to re-dissolving.

Remove the cathode, place it in a 250-ml beaker and dissolve the deposit by the dropwise addition of concentrated nitric acid. Wash the cathode, remove it, add 10 ml of 1 per cent. w/v ferric nitrate solution, an excess of ammonia solution, boil for 10 minutes and set aside in a hot place for 10 minutes.

Filter, washing away all the copper complex with an ammonia - ammonium nitrate - ammonium carbonate mixture. Dissolve the hydroxides in hot 10 per cent. v/v sulphuric acid, add 10 ml of 50 per cent. w/v potassium iodide solution and discharge the liberated iodine with 0.5 per cent. w/v sulphurous acid solution, adding 5 drops in excess. Boil for 10 minutes, filter off and wash the precipitated selenium and tellurium (omit if absent), and add 5 ml of 10 per cent. sodium hypophosphite solution to discharge the free iodine colour, leaving the yellow colour of the bismuth tri-iodide ion. Dilute to 100 ml with water and determine the bismuth content by means of a Spekker absorptiometer, using violet filters.

#### NOTES—

1. With samples of high bismuth content it will be found necessary to use an aliquot after dissolving the deposit from the cathode. During the electrolysis these samples generally, but not always, form a dark deposit. Provided that accurate procedure is used in preparing the aliquot, samples containing up to at least 5 per cent. of bismuth could be analysed by this method.
2. Use larger weights if necessary for samples with low bismuth content.
3. If the copper content of the sample is low, it must be added to the electrolyte before plating. The percentage of copper should be at least 50 times the percentage of bismuth present.

## RESULTS

Copper concentrates, mattes, feeds, tailings and blister copper with bismuth contents of between 0.0003 and 0.18 per cent. were analysed for bismuth by both the electrolytic and sulphide methods. Typical results were as follows—

Bismuth by electrolytic method, % ..	0.177	0.12	0.104	0.0006	0.0172	0.0009	0.0003
Bismuth by sulphide method, % ..	0.180	0.13	0.110	0.0006	0.0177	0.0009	0.0003

To 0.1-g portions of a sample containing 0.177 per cent. of bismuth were added various amounts of a standard bismuth sulphate solution (1 ml = 0.1 mg of bismuth). The results by the electrolytic method are shown in Table I.

TABLE I  
BISMUTH RECOVERY BY THE ELECTROLYTIC METHOD

Bismuth added, mg	Bismuth found, mg	Bismuth recovered, mg
0.000	0.176	0.000
0.050	0.225	0.049
0.100	0.271	0.095
0.150	0.320	0.144
0.200	0.372	0.196

## CONCLUSIONS

During the normal electrolytic determination of copper, small amounts of bismuth, if present, are deposited completely on the cathode. This fact considerably simplifies the bismuth determination. Due allowance should be made for the bismuth deposited on the cathode when determining copper electrolytically on samples containing bismuth, depending on the accuracy required.

I acknowledge my indebtedness to the Roan Antelope Copper Mines Limited, for permission to publish this method, and to the chemists in the laboratory, who carried out similar work in the past.

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6. —, *op. cit.*, p. 31.

## CHEMICAL LABORATORY

ROAN ANTELOPE COPPER MINES LIMITED  
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First submitted, July 11th, 1955  
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## Ministry of Agriculture, Fisheries and Food

## STATUTORY INSTRUMENTS\*

1956—No. 1166. The Food Standards (Curry Powder) (Amendment) Regulations, 1956.  
Price 3d.

These Regulations, which came into operation on August 2nd, 1956, apply in England and Wales only; they amend the Food Standards (Curry Powder) Order, 1949 (S.I., 1949, No. 1816; Analyst, 1950, 75, 112), by raising the limit of lead that may be present in curry powder from 10 parts per million to 20 parts per million.

1956—No. 1167. The Food Standards (Tomato Ketchup) (Amendment) Regulations, 1956.  
Price 3d.

These Regulations, which came into operation on August 2nd, 1956, apply in England and Wales only; they amend the Food Standards (Tomato Ketchup) Order, 1949 (S.I., 1949, No. 1817; Analyst, 1950, 75, 112) by substituting for the limit of 50 parts of copper per million parts of the dried total solids in tomato ketchup, catsup, sauce or relish a limit of 20 parts of copper per million parts of the tomato ketchup, catsup, sauce or relish as a whole.

\* Obtainable from H.M. Stationery Office. Italics indicate changed wording.

**1956—No. 1181. The Bread (Amendment No. 2) Order, 1956.** Price 3d.

*This Order, which comes into operation on September 30th, 1956, amends the Bread Order, 1953 (S.I., 1953, No. 1283; Analyst, 1953, 78, 566) as amended (S.I., 1955, No. 221; Analyst, 1955, 80, 240; and S.I., 1956, No. 217) by deleting many definitions in Article 2, the whole of articles 4 to 9 inclusive, 11 and 13, and the First and Second Schedules.*

**1956—No. 1182. The Flour (Revocation) Order, 1956.** Price 3d.

*This Order, which comes into operation on September 30th, 1956, revokes the Flour Order, 1953 (S.I., 1953, No. 1282; Analyst, 1953, 78, 566); modified requirements become operative on the same date under the Regulations noted below.*

**1956—No. 1183. The Flour (Composition) Regulations, 1956.** Price 3d.

*These Regulations, which come into operation on September 30th, 1956, prescribe compositional requirements as respects certain nutrients, viz., iron, vitamin B<sub>1</sub> and nicotinic acid or nicotinamide, in all flour and as respects *creta praeparata* in all flour other than flour containing the whole of the products derived from the milling of wheat.*

## British Standards Institution

### NEW SPECIFICATIONS\*

B.S. 2720:1956. Dipping Thermometer. Price 2s. 6d.

B.S. 2758:1956. Vegetable-parchment - Aluminium-foil Laminates (Parchfoil) for Wrapping Dairy and Other Food Products. Price 2s.

B.S. 2761:1956. Spherical Ground Glass Joints. Price 2s.

### AMENDMENT SLIPS\*

PRINTED slips bearing amendments to British Standards have been issued by the Institution as follows—

PD 2507—Amendment No. 3 (July, 1956) to B.S. 1425:1954. Cleanliness of Fillings and Stuffings.

PD 2513—Amendment No. 1 (July, 1956) to B.S. 611:1952. Petri Dishes.

PD 2517—Amendment No. 1 (June, 1956) to B.S. 2648:1955. Performance Requirements for Electrically-heated Laboratory Drying Ovens.

PD 2536—Amendment No. 1 (July, 1956) to B.S. 1427:1949. Tests for Water used in Steam Generation.

## Book Reviews

**ANALYSE QUALITATIVE MINÉRALE.** By PAUL-E. WENGER, Dr. ès Sc., DENYS MONNIER, Dr. ès Sc., and YVONNE RUSCONI. Pp. xviii + 315. Geneva: Georg et Cie, S. A. 1955. Price Sw. fr. 25.

Reasonably comprehensive textbooks on qualitative inorganic analysis, that is, textbooks that do not restrict themselves more or less to the familiar elements, are sufficiently uncommon to make this book of interest to those who read French. It is very compact, and its approach is, on the whole, the orthodox approach of classical analysis.

The first section, comprising about 60 pages, presents a concise account of the theory conventionally associated with qualitative analysis, with due regard to its development in the light of modern theories. Perhaps its very conciseness occasionally leads to statements or treatments that might be challenged, as in the treatment of the dissociation of electrolytes or the nomenclature of complexes. However, this section of the book will be of least moment to the English-speaking analyst, since a comparable section is common to most books in this field.

For the English reader most interest will be centred in the subsequent parts of the book. The so-called "descriptive" section devotes about 150 pages to the reactions of cations and a further 50 to the reactions of anions. These are grouped according to classical ideas, the cations, for example, being arranged in accordance with their order of appearance in the familiar sulphide separation.

Each ion is treated individually. There is a brief description, first of the element, then of the ion. A list of slightly soluble compounds is given, together with, where known, some numerical indication of the solubility. A table gives the more important analytical reactions of the ion, and finally details are given for one or more confirmatory tests for which the sensitivities and other

\* Obtainable from the British Standards Institution, Sales Department, 2 Park Street, London, W.1.

relevant information are quoted. It is of importance to note that this section of the book does not confine itself to the "familiar" cations and anions, but is quite comprehensive, about 60 cations and 40 anions being included.

The "practical" section, which completes the book, occupies another 50 pages, and deals first with the various techniques, macro or semi-micro, wet way or dry way, which the analyst may utilise. Here the brevity, coupled with the absence of illustrations, combine to give a section that would be of doubtful value to the beginner, but might more properly be regarded as an *aide mémor* for the more experienced worker. Separation tables follow. It is perhaps a pity that the principle of including the less familiar ions is not followed to the logical conclusion. An indication is given of the point of appearance of the less familiar cations, but full directions for separation are only given for some of these. However, the scheme as given is undoubtedly an advance on the conventional teaching form.

The book ends with a very useful section on the various methods for opening up a sample before analysis.

This book contains a fund of useful information on the modern approach to the classical procedures of qualitative analysis, on a broad and realistic basis. Undoubtedly there are matters (mostly of omission) with which the individual may disagree. But this does not prevent recognition of the service that the authors have done in presenting this fresh and stimulating account of a subject that tends to become hackneyed.

Particularly welcome is the warning, clearly conveyed to the reader, that qualitative analysis is no rule-of-thumb application of a rigid set of tables, but succeeds only when intelligence is combined with knowledge—that "le propre de l'analyste habile est, précisément, de savoir combiner sa méthode suivant les données des recherches préliminaires. Il ne faut donc considérer les tables que comme un schéma général de travail, indispensable au débutant et pouvant servir de guide à celui qui, suffisamment éduqué, peut les modifier selon les besoins." This book, in the reviewer's opinion, should be most valuable in converting the analyst from the "débutant" to him who is "suffisamment éduqué."

CECIL L. WILSON

**METHODS OF BIOCHEMICAL ANALYSIS. Volume III.** Edited by DAVID GLICK. Pp. x + 437. New York and London: Interscience Publishers Inc. 1956. Price \$9.50; 75s.

This third volume of an annual series is as interesting as it is useful. There are twelve articles each with many references, and there is also a cumulative index to the three volumes.

Lindberg and Ernster (Stockholm) review concisely the determination of organic phosphorus compounds by phosphate analysis and include *in vitro* systems. Stokstad (New York) and others discuss the assay of thioctic acid and conjugates by the use of *Tetrahymena* and various bacteria. The quantitative determination of histamine by biological and chemical methods is dealt with by Code (Mayo Clinic) and McIntire (Abbott Laboratories) and detailed procedures are recommended. Plesner and Kalckar (Copenhagen) deal with enzymic micro-determinations of uric acid, hypoxanthine, xanthine, adenine and xanthopterin by ultra-violet spectrophotometry and lay proper emphasis on the specificity of the enzymes used. Dyer (Wisconsin) contributes an interesting essay on the use of periodate oxidations in biochemical analysis, while Smith (Minnesota) with Montgomery (Iowa) deal fully with end-group analysis of polysaccharides; these two articles, however, make clear the primacy of methylation procedures. Barker, Bourne and Whiffen (Birmingham) review in detail the use of infra-red spectra in the determination of carbohydrate structure; this article is concerned with interpreting data and not with spectroscopic methods.

Schubert (Argonne National Laboratory) contributes a most interesting article on the measurement of complex-ion stability by the use of ion-exchange resins and draws attention to great advantages of the method. Hughes and Klotz (North Western) survey the methods available for studying the nature of the interactions of proteins with metal ions; the article has an authoritative account of the equilibrium dialysis method and also of the calculation of stoichiometry and energetics from binding data. Raaflaub (Zurich) has contributed an essay on the application of metal buffers and metal indicators in biochemistry, a subject developed in recent years by Schwarzenbach and not yet widely known. *Natrium citrate* appears in this section, but the editing is well-nigh perfect. Malmström (Uppsala) offers a very competent account of the determination of zinc in biological materials.

Flame photometry and spectrometry are dealt with by Margoshes and Vallee (Boston) in a manner that will help beginners and also stimulate workers experienced in the field.

All contributors to this series of volumes try to cater for two very different readers, one concerned to keep abreast in a general way with "developments and innovations of current interest" and the other concerned with carrying out in his own laboratory the operations described and recommended. That so many of the articles succeed in this dual aim is a considerable achievement.

R. A. MORTON

EXPERIMENTAL DESIGN AND ITS STATISTICAL BASIS. By D. J. FINNEY, M.A., Sc.D., F.R.S. Pp. xii + 169. London: Cambridge University Press. 1955. Price 30s.

Those acquainted with Dr. Finney's previous books, such as his "Probit Analysis" and "Statistical Method in Biological Assay," will expect the title of this new one to disclose its contents with considerable accuracy. They will indeed find that it is about what the title indicates and not about anything else. Its scope has been deliberately circumscribed so, it would seem, as to justify its appearance as one of a series under the general direction of the University of Chicago Committee on Publications in Biology and Medicine. The opening sentence of the author's foreword, moreover, reads "This book is an attempt to outline the theory and practice of that branch of statistical science generally known as *experimental design*, in a form that will be intelligible to students and research workers in most fields of biology."

It is therefore not surprising that there is in the book nothing to be found of obvious or direct interest to the analytical chemist. Nevertheless, the accepted inclusion of biological assay within the confines of chemical analysis makes it at least possible, if not indeed probable, that members of the Biological Methods Group may find some food for thought here, as perhaps may also those others who, in growing numbers, are becoming alive to the uses of statistical design and analysis for analytical investigations and for quality control, in the widest sense of that term. This likelihood is increased when we remember that the same basic principle of experimental design must apply throughout the sciences, even though the examples used here are almost exclusively chosen from biology.

The indirect relevance of Dr. Finney's exposition to the analyst's work may justify a review here less detailed than would be permissible for a book of designedly chemical application. It should be sufficient to call especial attention to the admirable apologia contained in Chapter I, "Why Statistics," which all who run the analytical race might read, mark and inwardly digest, and to record that the next six chapters describe, with appropriate biological examples, various techniques of statistical design and analysis, including Counts, Measurements, Block Designs and Factorial and Sequential Measurements.

Moreover, Chapter VIII, on Biological Assay, obviously the one most likely to have a practical bearing on the work of *Analyst* readers, will be the more appreciated the better the contents of the earlier chapters have been absorbed and digested. Dr. Finney's definition of biological assay is, however, rather wider than some of us would countenance, so that he is compelled by his own logic to include a purely qualitative achievement, the identification of blood groups by serological tests (his own example), because to do this quantitative methods are used and are improved in efficiency by the proper application of statistical techniques. However that may be, his discussion of the more restricted type of assays proper, as I prefer to regard them, in which comparing of a test sample with a standard preparation is made the basis of measuring an ingredient of the former in terms of the latter, leaves nothing to be desired in the way of clear thought and concise expression.

As a kind of coda to the whole suite of movements, Dr. Finney concludes with "The Selection of a Design," and here again returns to and expands what was the main theme of Chapter I. There follow four pages of References and a little over two of Index in a well conceived, well produced book living in every way up to the reputations of author, sponsoring committee and publisher.

A. L. BACHARACH

THE NATIONAL FORMULARY. Tenth Edition. Pp. xliv + 867. Washington, D.C.: American Pharmaceutical Association. 1955. Price \$9.00 (in U.S.A.); \$10.00 (elsewhere).

The scope and significance of this work was outlined in the review of the Ninth Edition (*Analyst*, 1951, 76, 322). This, the Tenth Edition, is the fourth to be published according to a plan adopted by the Council of the American Pharmaceutical Association in 1938 for the issue of revisions at five-year intervals. Titles for 259 drugs and preparations for which official standards

would not otherwise be provided have been added to N.F.X, and 242 items included in N.F.IX have been omitted. A number of monographs not carried over from the Fourteenth Edition of the United States Pharmacopoeia to the current Fifteenth Edition have been transferred to the National Formulary, a practice corresponding in this country to the transfer of standards from the British Pharmacopoeia to the British Pharmaceutical Codex.

Apart from its official function, the book is essentially analytical in interest and, wherever practicable, quantitative limits are imposed and useful procedures for assay are given; the determination of total tocopherols and non-alpha tocopherols in Mixed Tocopherols Concentrate is an interesting example.

N. L. ALLPORT

### Publications Received

THE CHEMISTRY OF PHENOLIC RESINS. By ROBERT W. MARTIN. Pp. xii + 298. New York: John Wiley & Sons Inc.; London: Chapman & Hall Ltd. 1956. Price \$9.50; 76s.

ORGANIC CHEMISTRY. By LOUIS F. FIESER and MARY FIESER. Third Edition. Pp. vi + 1112. New York: Reinhold Publishing Corporation; London: Chapman & Hall Ltd. 1956. Price \$6.25; 50s.

ULTRAVIOLET AND VISIBLE ABSORPTION SPECTRA. INDEX FOR 1930-1954. By HERBERT M. HERSHENON. Pp. xviii + 205. New York: Academic Press Inc.; London: Academic Books Ltd. 1956. Price \$10.00; 80s.

ANNUAL REPORT 1955-6. Pp. 259. London: British Standards Institution. 1956. Price 6s.

THE USE OF CHEMICAL ADDITIVES IN FOOD PROCESSING. Prepared by the Food Protection Committee of the Food and Nutrition Board. Pp. viii + 91. Washington 25, D.C.: National Academy of Sciences—National Research Council. 1956. Price \$2.00.

THE INTERNATIONAL JOURNAL OF APPLIED RADIATION AND ISOTOPES. Edited by P. C. AEBERSOLD (Oak Ridge), A. H. W. ATEN, jun. (Amsterdam), J. A. BUGHER (Washington), J. COURSAGE (Saclay), V. N. KONDRATIEV (Moscow), M. MAGAT (Paris), J. L. PUTMAN (Harwell), H. R. NELSON (Columbus) and H. SELIGMAN (Harwell). Volume I, Nos. 1/2, July, 1956. Pp. 144. London and New York: Pergamon Press Ltd. Subscription A (normal) 120s., \$17.00, per volume; subscription B (for individual subscriber's own use) 70s., \$9.80, per volume.

*A new journal.*

SUPPLEMENT TO BRITISH CHEMICALS AND THEIR MANUFACTURERS. Pp. 35. London: The Association of British Chemical Manufacturers. 1956. Gratis.

AN INTRODUCTION TO MODERN ORGANIC ANALYSIS. By SIDNEY SIGGIA and HANS J. STOLTEN. Pp. viii + 250. New York and London: Interscience Publishers Inc. 1956. Price \$4.50; 36s.

KWALITATIEVE CHEMISCHE ANALYSE. By Prof. Dr. C. J. VAN NIEUWENBURG and Ir. J. W. L. VAN LIGTEN. Fourth Edition. Pp. 326. Amsterdam: D. B. Centen's Uitgeversmaatschappij N.V. 1956. Price Fl. 14.50.

### Errata

MAY (1956) ISSUE, p. 303, Table II. The name of the substance in the 4th line should read "7:8-Dimethoxy-1-oxo-1:2-dihydro-2-thianaphthalene-3-carboxylic acid."

The formula for toluene-*p*-sulphonchloride should read " $C_7H_7O_2ClS$ ." The volume of 0.01 *N* sodium hydroxide used for this substance should read "3.25."

The following corrections should be made to the values for "Sulphur found, %" and "Sulphur required in theory, %" —

	Found	Required
Sulphanilic acid, $C_6H_7O_2NS$	for 18.5 read 18.0;	for 18.4 read 18.5
Thiourea, $CH_4N_2S$		for 41.6 read 42.1
Thiosemicarbazide hydrochloride, $CH_6N_3ClS$		for 25.7 read 25.1
Methyl ester . . . $C_{12}H_{12}O_5S$	for 11.5 read 11.4	
4-Methyl-1-nitrothioxanthone, $C_{14}H_9O_3NS$	for 12.3 read 12.2;	for 12.5 read 11.8

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